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Environmental Impact Statement: ES:P&I submission - Sorption and desorption of diverse contaminants of varying polarity in wastewater sludge with and without alum

117 words

In order to better manage risks from a diverse array of emerging contaminants penetrating through wastewater treatment plants, a more general understanding of the sorption properties of wastewater sludge is needed. Here we tested the sorption and desorption behaviour of nine diverse contaminants to sludge with and without alum. Alum is commonly used as a flocculant in wastewater, and the difference in sorption properties of alum-flocculated sludge and regular sludge remains under explored. Here we found that alum can substantially reduce the sorption properties of sludge. Further, from our measurements and a review of the literature, there appears general trend that the more polar (or mobile) a contaminant, the greater the diversity in sorption behaviour to sludge.

Sorption and desorption of diverse contaminants of varying polarity in wastewater sludge with and without alum

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Sewage sludge sorption and desorption measurements were conducted for nine diverse contaminants of varying polarity: caffeine, sulfamethoxazole, carbamazepine, atrazine, estradiol, ethinylestradiol, diclofenac, and, for the first time desethylatrazine and norethindrone. Two types of sorption behaviour were observed. Compounds with a log octanol-water partition coefficient, log K_{ow} , below 3 showed little or no sorption over 48 hours of shaking, while compounds with log K_{ow} over 3 showed 30 to 90% sorption within the first few minutes. After 6 hours of shaking, mass loss through suspected biotransformation became evident for some compounds. At the pH range considered (5.7 – 6.7), diclofenac (pKa 4.0, log K_{ow} 4.5) was the only compound in which pH dependent sorption could be quantified. Log sewage sludge-water distribution coefficients, log K_d , ranged from 0.2 to 2.9, and, as expected, increased with increasing log K_{ow} of the compound and organic carbon (OC) content of the sewage sludge. A sewage sludge precipitated with alum had a substantially lower K_d values, as well as lower OC content, compared to alum-free sludge. Desorption was studied by sequentially replacing supernatant water. With each water replacement, log K_d values tended to either remain similar (following a linear isotherm) or in some cases increase (following a Freundlich-type isotherm). The length of time required to restore equilibrium increased with each rinsing step. A literature review of reported K_d values compared well with the alum-free sludge data, but not the alum-sludge data. Sewage sludge K_d across the literature appear more consistent with increasing K_{ow} .

1. Introduction

Emerging contaminants (ECs) are substances whose presence in the environment is poorly understood but are of increasing interest because of potential ecological or human health risks.¹⁻⁵ ECs can come from any chemical compound class, including pharmaceuticals, personal care products, pesticides, surfactants and flame retardants.^{6, 7} Confronting ECs involves several analytical, conceptual and management challenges. Urban areas are primary emitters of ECs, and municipal wastewater treatment plants (WWTPs) are not designed for removing a broad array of contaminants.⁸ WWTPs can therefore release several ECs into recipient aquatic environments, or alternatively into soil environments when sewage sludge from WWTPs are used in land applications.⁹

To develop management strategies for ECs in WWTPs, the sorption of diverse ECs to diverse sludge types needs to be accounted for. In the present study three unique sludge types, including one containing the popular flocculant alum, were used to study the sorption and desorption behavior of nine

diverse ECs: caffeine (stimulant), sulfamethoxazole (antibiotic), atrazine (pesticide), desethylatrazine (degradation product of atrazine), carbamazepine (antiepileptic), estradiol, ethinylestradiol, norethindrone (hormones) and diclofenac (anti-inflammatory). Many of these ECs have been reported in WWTP sludge, including estradiol and ethinylestradiol,¹⁰ carbamazepine,¹¹ diclofenac,¹¹ caffeine¹² and sulfamethoxazole.¹³ Despite their presence in WWTPs, the sorption and desorption behavior of many of these compounds is poorly understood, particularly for desethylatrazine and norethindrone which are included in a sludge sorption study here for the first time. Further, the role of alum on sludge sorption has been seldom explored in the literature. The aim of this work is to better understand the sludge sorption behaviour of diverse ECs in order to improve WWTP management strategies.

2. Experimental

2.1. Chemicals

All selected compound standards (Table 1) (purity $\geq 97\%$) were obtained from Sigma-Aldrich Canada (Oakville, ON, Canada). Mass-labeled internal standards [$^{13}\text{C}_3$]-atrazine, [$^{13}\text{C}_2$]-ethinylestradiol, carbamazepine-d10, [$^{13}\text{C}_3$]-caffeine and [$^{13}\text{C}_6$]-sulfamethoxazole were supplied from Cambridge Isotope Laboratories, Inc. (Andover, MA). Diclofenac-d4 was obtained from C/D/N Isotopes (Pointe-Claire, QC, Canada). All solvents (trace analysis grade) were purchased from Fisher Scientific (Whitby, ON, Canada). Individual standard stock solutions (1000 mg L⁻¹) and the internal standard working solution (at a concentration of 2 mg L⁻¹) were prepared in methanol. A mixture of all individual standards at 2 mg L⁻¹ was prepared in methanol. All solutions were stored at -20 °C in amber glass bottles and kept for a maximum of 6 months.

Table 1. Target compounds and characteristics

Compound	MW	Log K_{ow} ^a	pK _a		
Atrazine	ATZ	215.69	2.61	3.2 ^b	(base)
Desethylatrazine	DEA	187.63	1.51	1.4 ^c	(base)
Estradiol	E2	272.39	4.01	10.33 ^b	(acid)
Ethinylestradiol	EE2	296.41	3.67	10.33 ^b	(acid)
Norethindrone	NOR	298.43	2.97	10.4 ¹⁴	(acid)
Carbamazepine	CBZ	236.28	2.45	15.96 ^b	(acid)
Caffeine	CAF	194.19	-0.07	-0.92 ^b	(base)
Sulfamethoxazole	SMX	253.28	0.89	6.16 ^b	(acid)
Diclofenac	DCF	296.16	4.51	4.00 ^b	(acid)

MW = molecular weight (g mol⁻¹), ^aEPI Suite v4.11¹⁵, ^bChemaxon data¹⁶

2.2 Sludge source

Wastewater sludge was obtained from two Canadian municipal wastewater treatment plants, here labelled WWTP-A and WWTP-B. The WWTP-A samples were collected from the primary clarifier sludge tank. Two WWTP-B samples were collected in a primary sedimentation tank, fed with raw wastewater, after grit removal. One of the WWTP-B samples contained alum, which was added as a coagulating agent, the other was alum-free (as was WWTP-A). The sludge characteristics are presented in Table 2. The pH of the sludges was determined for the filtered aqueous phase for each sorption experiment described below and averaged. The organic content was determined gravimetrically in duplicate by combustion (550 °C, 1h).

Table 2. Characteristics of sludge collected as a slurry (Mean \pm SD)

Source	pH	Total suspended solids (TSS) (g _{sludge} /L)	Organic content solid (f _{OC}) (%)	Organic content per sludge volume (g _{OC} /L)
WWTP-A	5.7 \pm 0.3	36.0 \pm 2.6	66 \pm 1	23.8
WWTP-B	5.6 \pm 0.1	19.3 \pm 2.7	73 \pm 2	14.1
WWTP-B-Alum	6.7 \pm 0.2	8.9 \pm 0.8	81 \pm 3	7.2

2.3 Sorption/desorption kinetics experiment

2.3.1. Sorption Kinetics Experiment. Following recommendations for sorption experiments by the Organisation for Economic Co-operation and Development to quantify sorption (as elaborated in the Supplementary Information (SI)),¹⁷ duplicate batches with 10 mL of well mixed sludge solution in 15-mL conical polypropylene centrifuge tubes were spiked (100 μL) with mixed standard solution to reach a concentration of 20 $\mu\text{g/L}$ and shaken on an orbital agitator for 48h. A previous study found negligible artifacts of the analyte ECs from using polypropylene tubes.¹⁸ This was validated here by use of control vials. For this, a sludge sample was centrifuged (at 220 g) and the supernatant was removed, filtered, placed in a control vial and spiked at the same concentration as the samples (described below). The control vials were placed on an orbital shaker for 48 h and then filtered and analysed as other samples.

Experiments were conducted at ambient temperature (≈ 22 °C). Sixteen identical tubes were prepared per sludge type, and at specified time intervals after placement on the orbital shaker, 5 min, 15 min, 30 min, 1 h, 2 h, 6 h, 24 h and 48 h, duplicate vials were removed, and the aqueous concentrations determined by filtering and instrumental analysis (as described below). For the 5 min and 48 h samples, the solid phase was also isolated for quantification by centrifuging at 220 g for 1 min and 20 min, respectively, removing the supernatant, freezing at -20 °C and then freeze-drying.

Aqueous samples were filtered using a 0.3 μm pore size glass fiber filter (Sterlitech Corporation, Kent, WA) to remove any residual particulate material. This filter was selected as appropriate, showing minimum loss of the selected analytes due to sorption on filters¹⁸. Filtered water samples were then diluted with MilliQ water (50 %) in order not to saturate the column and/or the detector. The samples were then acidified with formic acid (25 μL for 5 mL of aqueous phase, purity > 95%) and stored at 4 °C to avoid microbial growth until liquid chromatography atmospheric pressure chemical ionization coupled to tandem mass spectrometry (HPLC-APCI-MS/MS) analysis.

Dry sludge samples were extracted by sonication-assisted solvent extraction with a mixture of methanol and acetone 3:1 and evaporated to dryness¹⁸. The extracts were reconstituted to 4 mL with acidified water (0.1 % formic acid) containing 5 %

of MeOH. The internal standards were added to a final concentration of 5 µg/L. Extracts were sonicated to promote dissolution for 10 min at 30 °C, centrifuged for 10 min at 220 g, filtered as the aqueous samples, and analyzed by HPLC-APCI-MS/MS.

Mass balance was performed at the end of the experiment (48 hours) by measuring the concentration of the target ECs in both the aqueous phase and the sludge and comparing it to the spiked and initial amount (i.e. Mass Balance (%) = 100 x (Mass in water + Mass in sediment) / (Spiked Mass + Initial Mass in water + Initial Mass in sediment)). Note the 5 min centrifugation samples, however, were not considered appropriate for mass-balance calculations, due to the loss of particles from the samples during filtration.

2.3.2. Desorption kinetic experiments. Desorption studies of spiked sludges were carried out for all the 9 target contaminants. First, the sludges were spiked as in the sorption study, allowed to shake for 48 hours, centrifuged (20 min, 220 g), then 7 to 8 mL of supernatant was removed (ensuring that no particles were removed) and were replaced by a similar volume of clean tap water. The liquid/solid (L/S) ratio ranged from 0.02 to 0.04 L/g dry sludge, depending on the sludge source. The sludge samples were dispersed by agitation and the suspensions were shaken on an orbital agitator for 24h. The rinsing step was repeated three times for each sample to promote desorption. The supernatant was used to determine the concentration of the contaminants in the solution after each rinsing step. In the first step, entire samples (prepared as extra replicates) were centrifuged in duplicate after 1 and 6 h to monitor the evolution of their concentration in the solution. The mass balance was calculated at the end of the experiment by measuring their concentration in both the aqueous phase and the solids.

2.4 Instrumental analysis

The quantification HPLC-APCI-MS/MS system consists of an HTC thermopal autosampler (CTC analytics AG, Zwingen, Switzerland) with a 1-mL loop, a dual switching-column array and a liquid chromatography tandem mass spectrometry system. A quaternary pump Accela 600 (Thermo Finnigan, San Jose, CA) was used for sample loading onto an on-line Hypersil Gold C₁₈ column (20 mm x 2.1 mm, 12 µm particle size). The column switching system was made of six-port and ten-port valves (VICI® Valco Instruments Co. Inc., Houston, TX) described elsewhere.¹⁹ Elution was achieved using a quaternary pump Accela 1200 (Thermo Finnigan, San Jose, CA) and chromatographic separation was performed with a Hypersil Gold column (100 mm X 2.1 mm, 1.9 µm particle size) kept at 55 °C in a thermostated column compartment. Gradient elution conditions are shown in Table S1 in the SI. The analytical column was preceded by a guard column (2 X 2mm, 5mm) of the same packing material.

A TSQ Quantum Ultra AM triple quadrupole mass spectrometer (Thermo Fisher Scientific, Waltham, MA) with an atmospheric pressure chemical ionisation (APCI) source was

used for detection and quantification. This was operated in selected reaction monitoring mode and the ionization was achieved in positive mode. The initial compound-dependent parameters for MS and MS/MS optimization conditions are presented in Table S2. The source-dependent parameters were as follows: discharge current (5 µA), vaporizer temperature (490 °C), sheath gas pressure (50 arbitrary units), auxiliary gas pressure (15 arbitrary units), ion sweep gas pressure (0 arbitrary units) and capillary temperature (350 °C). Scan time was adjusted to 0.007s. The first and third quadrupole were operated at 0.7 Da FWHM and the collision gas pressure was set at 1.5 mTorr. The identification of target analytes was done by using two selected reaction monitoring transitions (SRM) with their relative intensities. Quantification used the most abundant product ion and confirmation used the second most abundant ion.

2.5 Quality assurance and control

Method performance was evaluated using filtered tap water as a reference media. The limits of detection (LOD), limits of quantification (LOQ), linearity and precision were determined using a six to ten point calibration curve, analyzed in duplicate, in tap water and in wastewater. The correlation coefficients (r²) were deemed satisfactory, ranging from 0.9983 to 1.0000 in tap water and from 0.9979 to 0.9998 in wastewater. The LOD and LOQ were determined with the measurement of signal to noise (S/N) ratio. The S/N ratios used were respectively 3 and 10. LODs ranged from 0.5 to 20 ng/L in tap water and from 15 to 115 ng/L in wastewater, as summarized in Table S3. The repeatability (intra-day, n=5) and reproducibility (inter-day, n=3) of the method varied from 2 to 15% (see Table S4). Since wastewater is a complex matrix, matrix effects (i.e ion suppression/enhancement) is generally observed, explaining the variation in the different validation parameters.²⁰

The extraction recoveries of the solid particles were performed at two concentration levels (50 and 200 ng/g) on a composite of the three sludge samples used in this study. As caffeine was naturally present in the sludge at high levels (> 400 ng/g), it was decided to adjust the spiked amount of caffeine to 500 ng/g for the first level and to 2000 ng/g for the second level to make sure that the addition was significant compared to the initial concentration. The recoveries were in the range 60-103 % (Table S5), which is consistent with those obtained earlier.¹⁸

3. Results and discussion

3.1. Mass balance

Mass balance was determined at the end of each sorption and desorption experiment (Table S6). Results vary depending on the compound. The greatest mass loss was for estradiol (E2) (ranging from 7±7 to 21±8%). Variable ranges of mass loss were observed for norethindrone (NOR) (ranging from 18±32 to 63±15%), sulfamethoxazole (SMX) (ranging from 25±45 to 82±13%) ethinylestradiol (EE2) (ranging from 44±2 to

51±19%) and diclofenac (DCF) (ranging from 57±15 to 69±18%). Mass losses for the other compounds, atrazine (ATZ), desethylatrazine (DEA), carbamazepine (CBZ) and caffeine (CAF) were not statistically different from 90%. This lack of complete recovery for some compounds is likely due to microbial transformation. Previous studies have reported that biotransformation in a WWTP can account for more aqueous phase losses than sorption to sewage sludge for certain antibiotics, pharmaceuticals and musks.²¹⁻²³ E2 is often observed to readily biotransform to estrone in sludge²⁴. Biotransformation of EE2, SMX and DCF has also been observed, but found to be highly variable, and dependant on treatment.²⁵⁻²⁸ CBZ has been found to be stable during treatment in sludges.²⁸ The biggest inconsistency with the literature is the observed stability of CAF, as other studies have reported rapid biotransformation of CAF in sludge.²⁶ To our knowledge, the biotransformation of NOR, ATZ and DEA in sewage sludge has not been studied.

3.2 Sorption behavior and compound K_{ow}

The decrease in the aqueous concentration (C_w) with time after spiking is presented in Figures 1-2 and in Figures S1-S9 in the SI, with raw data in Tables S7-16. The decrease of C_w over time (when observed) is due to both sorption and mass loss processes such as biotransformation, with mass loss after 48 hours being particularly influential for E2, NOR and SMX. Figure 1 presents trends for CAF, ATZ and E2 using the WWTP-B sludge as representative of compounds with different log K_{ow} (low: CAF -0.07, intermediate: ATZ 2.61, high: E2 4.01). Compounds with higher log K_{ow} are generally assumed to sorb onto organic matter with greater affinity than those with low K_{ow} .³⁰⁻³² Here, the compounds with high log K_{ow} (≥ 3), DCF together with the three hormones (E2, EE2 and NOR) exhibited rapid decreases in C_w followed by slow decreases in C_w (Figures 1, 2c, S4-6), with 30 to 90% of the initial added C_w removed from water during the first five minutes, and then at a slower rate afterwards. This could indicate a biphasic sorption uptake (such as first surface adsorption followed by bulk-phase absorption). However, here, it is suspected that this slow decrease is additionally influenced by biotransformation²⁵, based on the observed mass loss.

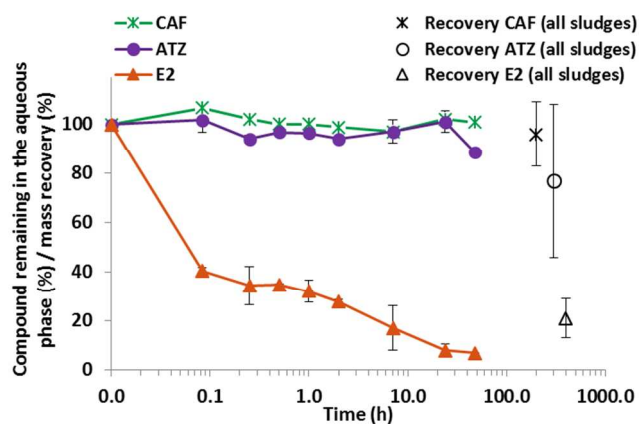


Figure 1. Aqueous phase concentration remaining vs time shaken after spiking for caffeine, atrazine and estradiol in the WWTP-B sludge

Regarding the compounds with lower log K_{ow} (< 3 , i.e. CAF, SMX, DEA, ATZ and CBZ) negligible to minor decreases in C_w occur in the first 6 hours; however, after 6 hours substantial decreases are observed for SMX in all three sludges and DEA in one sludge. The decrease after 6 hours of shaking observed for these systems is suspected of being due to biotransformation (or other mass loss processes) and not sorption, given the relatively low mass balances in these systems, low sorption being expected (low K_{ow}), and no

instantaneous sorption being observed.²⁴

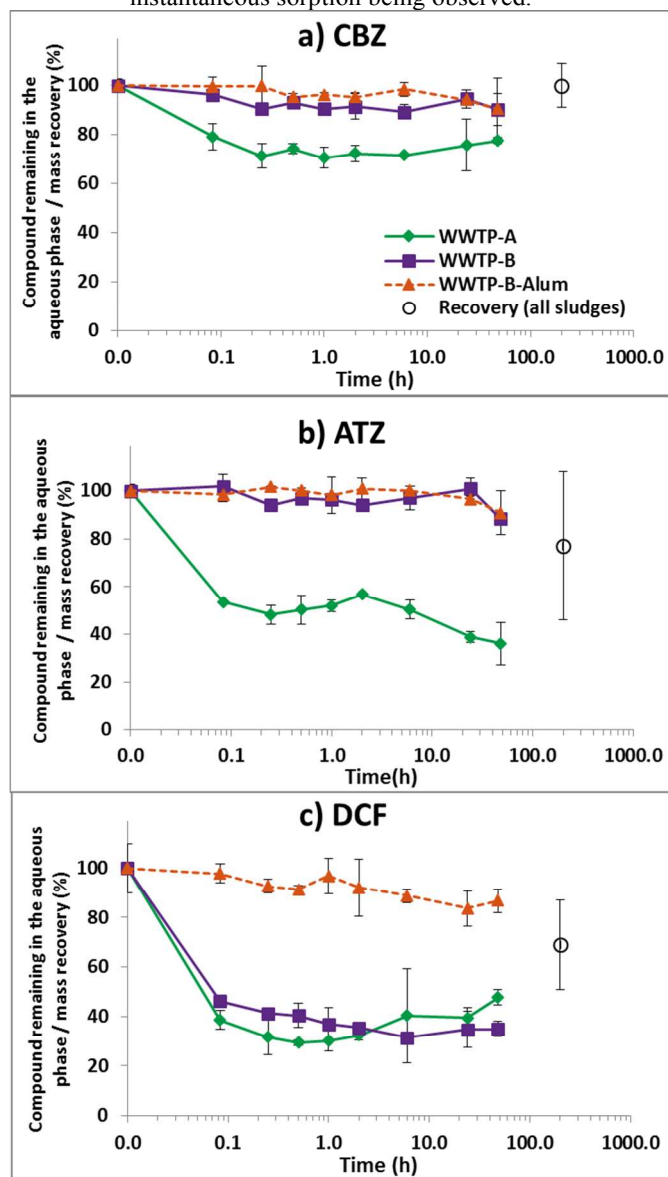


Figure 2. Aqueous phase concentration remaining after spiking vs shaking time for a) carbamazepine b) atrazine and c) diclofenac in the three different sludge samples.

3.3 Sorption behavior and OC content

Sorption of organic compounds to soils and sediments generally increases with increasing OC.³² As presented in Table 2, samples coming from WWTP-A are the richest in OC per volume of wet sludge (24 g_{OC}/L_{sludge}), followed by WWTP-B (14 g_{OC}/L_{sludge}) and WWTP-B-Alum (7 g_{OC}/L_{sludge}). Based on this, it is expected that the WWTP-A sludge would sorb the most and WWTP-B-Alum the least. As evident from Figures 2, S1-S9, this was observed here. For CBZ (Figure 2a) and ATZ (Figure 2b), which have an intermediate log K_{ow} (CBZ: 2.45, ATZ: 2.61), no significant sorption occurred in the two WWTP-B samples, but did for the WWTP-A samples (for CBZ around 20 % at 30 minutes and for ATZ around 50 % at 30 minutes). DCF (Figure 2c, log K_{ow} = 4.5) did not sorb

substantially to WWTP-B-Alum (though this is also influenced by pH, see the next section).

3.4 Changes induced by pH differences

Water pH can influence the surface charge of the sludges and the ionization of many ECs. From Table 2, the aqueous phase pH of WWTP-B-Alum is one unit higher (pH 6.7) than the two other sludge samples (pH 5.7, pH 5.6). Coagulation with alum is optimal when the pH is between 5.8 - 6.5³⁴, thus WWTP-B-alum pH was likely adjusted to 6.7 in the WWTP. Of the selected ECs, only SMX and DCF exhibit acid-dissociating constants, p K_a , in the range of the sludges (Table 1, SMX p K_a = 6.16, DCF p K_a = 4.00). The effect of the pH on the sorption of acidic analytes can be estimated using the pH-dependent octanol-water distribution coefficient (log D_{ow}).¹⁶

$$\log D_{ow} = \log K_{ow} + \log \frac{1}{1 + 10^{pH - pK_a}} \quad (1)$$

For SMX, log D_{ow} would change from 0.8 to 0.2 when increasing the pH from 5.7 to 6.7, implying that the negligible sorption occurring for the WWTP-A and WWTP-B sludges would be even less for the WWTP-B-Alum sludge, which agrees with the measured data (Figure S2). For DCF the log D_{ow} is 2.8 at pH 5.7 and 1.8 at pH 6.7. Thus, in the WWTP-B-Alum sludge treatment, DCF is expected to sorb less than the WWTP-A and WWTP-B sludges, which agrees with observations (Figure 2c).

3.5 Desorption experiments

The results from the desorption studies are presented for EE2 in Figure 3, with similar graphs for other compounds in the SI (Figures S7-S14).

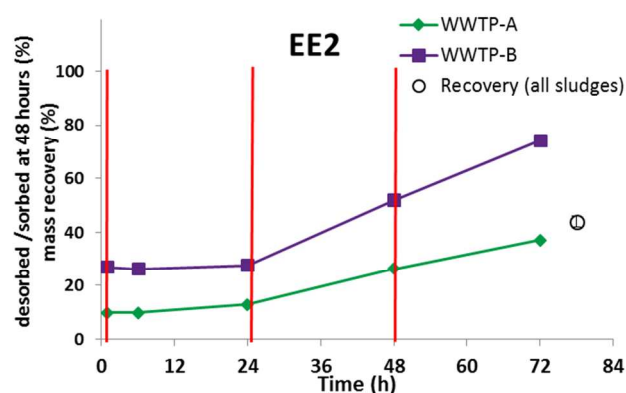


Figure 3. Cumulative desorption of ethinylestradiol in the two different sludge samples as a function of time and rinsing step (indicated by vertical lines) relative to the amount sorbed, and mass recovery compared to the original spiked amount (here EE2 had a similar mass balance in both sludges, but it desorbs more readily from WWTP-B).

In these Figures, the x-axis represents time, and the vertical lines crossing the x-axis indicate times when the supernatant water was removed and replaced with clean tap water. The y-axis presents the percentage of contaminant that appears in the

aqueous phase cumulatively compared to the initial sorbed amount; thus, 100% represents complete desorption in the absence of mass loss due to suspected biotransformation. Correspondingly, compounds with low mass balance due to suspected biotransformation (e.g. SMX, E2, NOR) will not reach 100% on the y-axis. As evident in these figures, compounds that did not substantially sorb, CAF, DEA, CBZ and ATZ (Figures S7-10) desorbed easily, reaching 80 – 100 % desorption as a result of the treatment. SMX also appeared to desorb readily, though only 20-40 % mass was recovered due to suspected biotransformation. For compounds that exhibited relatively higher sorption, 50-70 % could be recovered after desorption and suspected biotransformation for E2, EE2 and DCF, whereas for NOR only 0 – 30% could be recovered.

The amount of contaminant removed per rinsing step is presented in the SI (Table S27). The released concentration tends to decrease in each dilution step, as less compound became available for desorption. For some compounds (DEA, CBZ, ATZ, E2, NOR), a minor re-sorption is often observed over the first 24 h period, as evident on Figures S7-14 with a downward slope at this interval, indicating equilibrium is being restored. In the subsequent water replacements, these low sorbing compounds continue to desorb after 24 hours, indicating that it takes longer to reach partitioning equilibrium per dilution step.

3.6 Instant sorption rates and dilution factors

As presented above, observable sorption for compounds with $\log K_{ow} > 3$ occurred within the first 5 minutes, with subsequent changes mainly attributable to both sorption and mass loss. Thus, in Table 3 the apparent sorption rate, $rate_{5-min}$, and rate constants, k_{5-min} , observed in the first time step of 5 minutes are presented, by use of the following equations:

$$rate_{5-min} (\text{ng g}^{-1} \text{min}^{-1}) = \frac{C_{S,5-min} - C_{S,0-min}}{5 \text{ min}} \quad (2)$$

$$k_{5-min} = \frac{-\log(C_{A,5-min}/C_{A,0-min})}{5 \text{ min}} \quad (3)$$

Where $C_{S,5-min}$, $C_{A,5-min}$, $C_{S,0-min}$ and $C_{A,0min}$ are the sludge (S) and aqueous (A) concentrations at 5 minutes (5-min) and initially (0-min). Rate constants could be derived for the hormones (E2, EE2 and NOR) and DCF in all sludge samples, as well as for ATZ and CBZ in the WWTP-A sludge. From Table 3, the hormones and DCF exhibited nearly identical 5-minute sorption rates in WWTP-B (98 – 162 $\text{ng g}^{-1} \text{min}^{-1}$), though for the WWTP-B-Alum, DCF exhibited much slower sorption rates than the hormones (9 vs. 79 – 235 $\text{ng g}^{-1} \text{min}^{-1}$). The results for WWTP-A are between these extremes (46 vs. 81 – 107 $\text{ng g}^{-1} \text{min}^{-1}$). The varying results for DCF are related to differences in pH (DCF is more present in the low sorbing ionic form in WWTP-B-Alum), as well as differences in sludge properties (OC, porosity, etc.).

Table 3. Sorption rates ($rate_{5-min}$, $\text{ng g}^{-1} \text{min}^{-1}$) and rate constants (k_{5-min} , min^{-1}) for the first five minutes after contaminant spiking.

Compound	WWTP-A		WWTP-B		WWTP-B-Alum	
	$rate_{5-min}$	k_{5-min}	$rate_{5-min}$	k_{5-min}	$rate_{5-min}$	k_{5-min}
E2	94	0.141	108	0.079	235	0.031
EE2	107	0.200	162	0.128	267	0.074
NOR	81	0.094	98	0.043	79	0.016
DCF	46	0.083	102	0.067	9	0.002
ATZ	59	0.054	sorption < LOQ		sorption < LOQ	
CBZ	27	0.020	sorption < LOQ		sorption < LOQ	

LOQ = limit of quantification

Regarding the removal of spiked contaminant through dilution; desorption/removal rate constants could not be determined. Desorption rate constants for DCF and CBZ of 0.07 min^{-1} have been previously reported³⁵ and are quite close to the sorption k_{5-min} we found for DCF in WWTP-A (0.083 min^{-1}) and WWTP-B (0.067 min^{-1}), but not WWTP-B alum (0.002 min^{-1}). This literature value for CBZ is reasonably close to k_{5-min} for WWTP-A (0.02 min^{-1}). Note that as the sorption rate slows down rapidly in the initial minutes, these rate constants should only be used to describe the first minutes of exposure of sludge to contaminated wastewater.

3.7. Sludge-water distribution coefficients

Solid water distribution coefficients (K_d , L kg^{-1}) can be used to describe the partitioning of contaminants between sludge and water within a wastewater treatment plant.³⁶ They are defined as the ratio of contaminant concentration in the solid (or sludge) phase (C_s , $\mu\text{g kg}_{\text{dw sludge}}^{-1}$) to the contaminant concentration in the aqueous phase (C_w , $\mu\text{g L}^{-1}$) in a system that has reached equilibrium.³⁷

$$K_d = \frac{C_s}{C_w} \quad (4)$$

This coefficient is generally normalised to the mass fraction of organic carbon in the solids, f_{oc} (%), using equation 5.³⁸

$$K_{oc} = \frac{K_d}{f_{oc}} \times 100 \quad (5)$$

As observed, sorption is almost instantaneous, K_d was calculated based on data after 5 minutes, which is considered a reasonable estimation of steady-state conditions in this system. The values obtained are shown in Table 4, and plotted in Figure 4.

Table 4. Logarithms of five-minute solid water distribution coefficients, K_d , and organic carbon normalized K_d , K_{OC} of selected compounds in the three sludge samples presented here and an overview of literature values.

Cmpd.	WWTP log K_d (this study)			Literature log K_d ^{a)}		
	A	B	B-Alum	min - max	avg. \pm s.d. ^{b)}	n sludges (n refs.) ^{c)}
CAF	0.8	0.9	0.6	0.9 - 3.1	1.9 \pm 0.4	11 (4)
SMX	0.8	-0.1	-0.3	0.4 - 2.6	2.0 \pm 0.7	28 (11)
CBZ	1.0	1.0	0.0	0.1 - 2.5	1.5 \pm 0.9	20 (9)
ATZ	1.4	0.5	-0.1	0.7 - 2.1	1.6 \pm 0.7	6 (3)
DEA	-0.3	0.1	-0.2			n.a.
E2	2.1	1.9	1.4	1.2 - 2.9	2.5 \pm 0.3	24 (12)
EE2	2.4	2.3	1.9	2.3 - 3.7	2.9 \pm 0.3	36 (14)
NOR	1.8	1.6	1.0			n.a.
DCF	1.7	1.8	0.1	1.2 - 3.1	2.0 \pm 0.4	17 (7)

Cmpd.	WWTP log K_{OC} (this study)			Literature log K_{OC} ^{a)}		
	A	B	B-Alum	min - max	avg. \pm s.d. ^{b)}	n sludges (n refs.) ^{c)}
CAF	1.0	1.1	0.7			
SMX	1.0	0.1	-0.3	1.6 - 2.8	2.2 \pm 0.6	6 (3)
CBZ	1.2	1.1	0.1	0.5 - 2.6	1.8 \pm 0.7	10 (5)
ATZ	1.6	0.6	0.0	1.7 - 2.4	1.9 \pm 0.3	6 (3)
DEA	-0.2	0.2	-0.1			n.a.
E2	2.3	2.0	1.5	2.8 - 3.3	3.2 \pm 0.1	8 (5)
EE2	2.6	2.4	2.0	2.8 - 3.5	3.2 \pm 0.2	11 (5)
NOR	2.0	1.7	1.1			n.a.
DCF	1.9	1.9	0.2	1.7 - 3.1	2.4 \pm 0.1	6 (3)

Cmpd = compound, n.a. = not applicable (not in the literature). a) K_d and K_{OC} of a wide range of primary, treated, activated, thickened and digested sludges from diverse locations and water treatment plants, a more detailed list can be found in the SI. b) Avg. and s.d. refer to the arithmetic average and standard deviation of log K values for unique sludge types, such that if multiple data existed for a specific sludge type within one publication, the average of this was used, and averaged with similar values from other literature sources. c) n sludges = number of unique sludge types (based on location and treatment), (refs) = number of unique peer-reviewed publications (as listed in the SI)

Based on the aforementioned role of OC, the K_d values for WWTP-B-Alum are the lowest (Table 4), due to it having the smallest f_{OC} (Table 2) A previous study recommended to add alum or other coagulating agents to precipitate hormones into sludge.³⁹ The results of the present study indicate that though alum may increase the amount of sludge and thus the amount of hormones co-precipitated, on a per mass basis, alum-flocculated sludge sorbs less intensely than non-flocculated sludge.

In Table 4 and Figure 5, the K_d values obtained in the present study are compared with the range of all known literature values (individually compiled in the SI-Section S7). Note that the amount of literature sorption data varies for the different ECs, from EE2 (17 studies) to DEA and NOR (measured here for the first time). It should be emphasized that

these literature values are for a wide variety of locations and sludge types (primary, secondary, thickened, activated, anaerobic etc.) and for various treatments (alkaline, thermal, ozone, etc.), as well as different wastewater origins (industry, urban, etc.) (for an overview, see SI-Table S10).

When comparing sorption data across such diverse sludges, it should also be considered that many diverse parameters can influence sorption in addition to OC. This is particularly the case for ionizable and polar compounds, where the ion-exchange capacity, surface area (i.e. floc size), surface charge and particle size can play an important role,^{40, 41} as well as competition with inorganic ions in the aqueous phase for ion-exchange sites on the sludge.⁴² Further, the presence of OC subfractions are also important to consider. Up to 15% of sludge OC can consist of exocellular polymeric substances (EPS) produced by bacteria, which have protein or the polysaccharide subdomains that can make differing hydrophobic and hydrophilic sorption interactions with compounds.⁴³ To account for the multiple type of sorption interactions that can occur between OC and sludge, multi-parameter type models have been suggested as the way forward.^{40, 44, 45} However, it should be noted that for such models, better characterisation of sludges would be needed than just f_{OC} .

For the most part, the obtained K_d values in this study were within the range of previously measured literature values, with the exception of caffeine and values for alum-flocculated WWTP-alum sludge, which generally tended to be on the low side of the previously reported ranges.

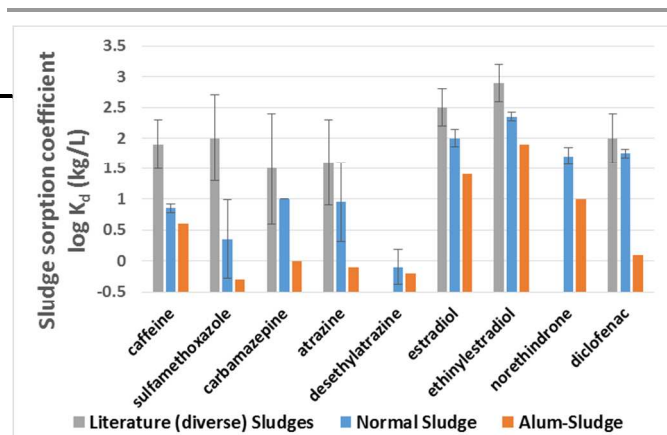


Figure 4. Comparison of average literature log K_d values and standard deviations (error bars) and those measured in this study for the test analytes. Note the literature log K_d are an average of the average values in individual citations, to avoid biasing citations with multiple sludges through similar methods. No literature data are available for desethylatrazine and norethindrone. As evident, hormones and diclofenac have relatively low standard deviations, unlike more polar compounds (i.e. with lower log K_{ow}). Also, the K_d values for alum-sludges are consistently the smallest.

A general trend from Table 4 and Figure 4 is that compounds with higher K_{ow} values (e.g. hormones) have more consistent log K_d and K_{OC} values across the literature compared to the compounds with lower K_{ow} values. For instance, the

standard deviation of log K_{OC} for E2, EE2 and DCF range from 0.1 – 0.2, whereas for the other compounds, the standard deviation ranges from 0.3 – 0.7. This indicates that the sorption to sludges becomes more heterogeneous as compound polarity increases (i.e. as hydrophobicity decreases), attributable to the increased variability of hydrophilic and ion-exchange interactions that can occur.^{41, 42, 44, 45}

In Table S27, desorption K_d values were derived for various time steps and compared to the 5-minute sorption K_d values. Trends in K_d with desorption and rinsing events were not consistent for all sludges and compounds. For the WWTP-B sludge, the K_d increased with desorption (except for E2 and EE2). For the WWTP-A sludge, K_d values either remained similar or slightly increased. Previous studies reported that the K_d of contaminants to sewage sludge slightly increases with desorption (i.e. within a factor 1.5).⁴⁶⁻⁴⁸ Examples of desorption log K_d vs. freshly spiked log K_d for SMX are 1.67 vs. 1.46 or 1.64 vs. 1.51, respectively,^{46, 47} and for EE2 are 2.74 vs 2.67 or 2.79 vs 2.51, respectively.^{47, 48} Collectively, this indicates that K_d values generally either stay the same or mildly increase with contaminant desorption. Following a Freundlich-type sorption paradigm, this is related to weaker sorption sites being depleted preferably to strong sorption sites on the sludge.

Conclusions

Accounting for the sorption and desorption behavior of diverse ECs to sewage sludge in WWTPs and the environment is challenging given the large heterogeneity of ECs and sewage sludge. However, for the use of designing effective WWTP remediation strategies one can consider certain generic behaviors based on simple parameters like the pH, K_{ow} , OC content and the use of alum. For the selected ECs in this study, which range in log K_{ow} from 0 – 4.5 some generalizations can be made: Sorption reaches an apparent steady-state within minutes of shaking. Compounds most likely to go through WWTP without effective removal are polar, persistent compounds, such as caffeine, atrazine and desethylatrazine. K_d values generally increases with K_{ow} and sludge OC. The difference between initial and desorbed K_d values, even in the literature, appears minor, though slightly increases with desorption. Alum appears to produce sludges that have a decreased sorption potential on a per mass basis, which may be worth following up on in future studies, as this could limit strategies of EC removal through flocculation. The heterogeneity of literature K_d values appears to decrease with increasing K_{ow} , thus, K_d values for more mobile, i.e. polar and ionic, compounds are likely to be quite variable. For the goal of removing mobile polar and ionic ECs from effluent water, further research on the roles of specific interactions to sludge, including the roles of solution chemistry and sludge heterogeneity, is needed.

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