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Degradation and sorption of commonly detected PPCPs in wetland sediments under aerobic and anaerobic conditions

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Abstract
Purpose Wetlands are a popular tool to treat/polish wastewater by reducing nutrient loading into the environment. In addition to nutrients, organic contaminants, such as pharmaceuticals and personal care products (PPCPs), are commonly detected in treated wastewater. Treatment wetlands may reduce concentrations of PPCPs before the treated effluent enters rivers and streams. Oxygen status may greatly affect the attenuation of PPCPs in wetland sediments by influencing microbial makeup and activity. An understanding of the effect of redox conditions on the degradation of PPCPs and the factors influencing PPCP sorption to wetland sediments is needed to maximize PPCP removal in treatment wetlands.
Materials and methods Three wetland sediments from the San Diego Creek and Newport Bay watershed in Southern California, USA, were incubated under aerobic and anaerobic conditions to assess the degradation of several regularly occurring PPCPs and their phase distribution as a function of time.
Results and discussion Under aerobic conditions, ibuprofen, *N*,*N*-diethyl-meta-toluamide (DEET), and gemfibrozil generally had half-life values around 20 days, while the half-life of carbamazepine was substantially longer (between 165 and 264 days). The anaerobic half-lives of gemfibrozil and ibuprofen increased by factors of 11–34 and carbamazepine increased by factors of 1.5–2.5. There was no detectable anaerobic degradation of DEET. The apparent phase distribution coefficient increased over time for DEET, carbamazepine and gemfibrozil, indicating that sorption of PPCPs to wetland sediments may be more limited than that predicted using equilibrium sorption coefficient values.
Conclusions Knowledge of the capacity of wetland sediments for degrading and sorbing PPCPs is vital to the design of treatment wetlands. Degradation of the selected PPCPs was enhanced under aerobic conditions as compared to anaerobic conditions. Sorption to sediments increased with contact time, indicating that longer hydraulic retention will increase wetland capabilities for removing PPCPs.

Keywords Carbamazepine · DEET · PPCPs · Wastewater treatment · Wetland

1 Introduction

While the ecosystem services of wetlands were once largely ignored, their true social, environmental, economic and esthetic values are now being increasingly recognized. Wetlands are ecosystems that possess remarkably variable physical and chemical characteristics. This heterogeneity creates an environment that is advantageous for the treatment of a wide range of environmental contaminants. Around the globe, the capabilities of wetlands (both natural and constructed) to cleanse water are being utilized to treat municipal wastewater. Traditionally, wetland treatment involved the removal and processing of nutrients and reductions in biological oxygen demand (Day et al. 2004), but in recent years, wetlands have also been shown to degrade and remove organic contaminants (Conkle et al. 2008; Matamoros et al. 2008).

A wealth of research over the last decade has demonstrated the common environmental occurrence of disinfection

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byproducts, flame retardants, and pharmaceutical and personal care products (PPCPs) due to the discharge of treated wastewater (Kasprzyk-Hordern et al. 2009; Matamoros et al. 2009a; Buth et al. 2010; Clarke et al. 2010). Although research has yet to establish a concrete link between the presence of these compounds with adverse effects to humans (Webb et al. 2003), numerous studies have demonstrated the negative effects that these compounds have on aquatic organisms (Jobling et al. 1998; Robinson et al. 2005; Chambers and Leiker 2006; Quinn et al. 2009). Therefore, it is imperative to explore mitigation practices that can cost-effectively remove these contaminants before they enter the open environment.

In smaller communities or areas where the costs of construction and maintenance of elaborate wastewater treatment facilities are not feasible, wetlands are often used to decrease nutrients and "polish" wastewater before it is discharged into the environment. White et al. (2006) suggested that wetlands may be a cheap and effective way for smaller communities to address the concern of PPCPs in their wastewater effluent. Research is urgently needed to understand the specific physicochemical properties of wetlands that affect PPCP degradation and sorption, the two processes that are likely most responsible for contaminant removal in wetlands.

Some PPCPs are known to be more persistent in sediment or water (e.g., carbamazepine and sulfamethoxazole), while others appear to be readily degradable (e.g., ibuprofen) following discharge (Heberer et al. 2002; Drillia et al. 2005; Conkle et al. 2008; Matamoros et al. 2009b). It is important to understand degradation of commonly occurring PPCPs in a variety of wetland sediments and discern the conditions that promote or inhibit such degradation. In addition, water retention times in treatment wetlands may vary widely but can be as short as 4–10 h (Matamoros et al. 2007, 2010). Therefore, the residence time may be too short for PPCPs to reach partition equilibrium between the water column and the wetland sediment, which dictates the need to determine phase partitioning as a function of contact time. Such knowledge, in turn, may be used to increase the performance of wetlands for retaining and attenuating PPCPs in wastewater effluents.

1.1 Objectives

The half-lives ($t_{1/2}$) of four commonly occurring PPCPs, i.e. carbamazepine, ibuprofen, gemfibrozil and *N*,*N*-diethyl-meta-toluamide (DEET), in three wetland sediments were measured in incubation experiments under aerobic and anaerobic conditions. To understand the distribution of PPCPs between water and sediment phases as a function of contact time, the apparent sediment/water phase distribution factor (K_d') was estimated for each PPCP at each time interval. The data collected in this study will be useful for optimizing the performance of wetlands when removing PPCPs by providing a better understanding of the effects of oxygen status and retention times.

2 Materials and methods

2.1 Chemicals

Standards of unlabeled DEET (insect repellent, 97 %), carbamazepine (antiepileptic, >98 %), ibuprofen (non-steroidal anti-inflammatory, >97 %), and gemfibrozil (fibrate, >99 %), were purchased from Sigma-Aldrich (St. Louis, MO, USA). Standards of deuterium-labeled ibuprofen-*d*3 (98 %) and gemfibrozil-*d*6 (98 %) were purchased from Toronto Research Chemicals (North York, ON, Canada). Standards of deuterium-labeled DEET-*d*7 (98 %), and carbamazepine-*d*10 (>99 %) were purchased from C/D/N Isotopes (Pointe-Claire, QC, Canada). Other chemicals used in this study were purchased from Sigma-Aldrich or Fisher Scientific (Fair Lawn, NJ, USA). Individual PPCP stock solutions (10 and 100 mg l^{-1} for each compound) were prepared in methanol and used to create standards for calibration curves ranging from 0.5 to 200 μg l^{-1}.

2.2 Sediment collection and characterization

Surface sediment (0–10 cm) from a 2 m^2 area was collected from three wetland sites (Newport Bay (NB), 11S 417966.67 m E 3721663.55 m; San Diego Creek (SD), 11S 419693.55 m E 3723856.39 m; Irvine Ranch Water District Constructed Wetland (CW), 11S 421489.55 m E 3725189.78 m) within the San Diego Creek Watershed in Orange County, CA, USA in late January and early February of 2011. After sampling, the sediment was immediately taken to the laboratory where it was homogenized and wet sieved (<1 mm) to remove debris and ensure uniform grain size. All sediments were stored at 4°C until use. Sediment properties such as moisture content, carbon content (loss on ignition), cation exchange capacity, and sediment pH were analyzed using standard methods (Table 1). The pH of the aqueous phase at each sampling interval was also measured for each sediment type in separate replicates with and without PPCP compound spikes. Different samples were used to measure pH to avoid cross contamination of samples. Prior to their use, each sediment type was tested for background levels of the compounds of interest with the extraction and analytical procedures (described below). There were no detectable amounts of any compound.

2.3 Sediment incubation under aerobic and anaerobic conditions

Aerobic degradation samples were prepared for each sediment type using 40 ml amber glass jars. Field moist sediments (10 g

Table 1 Sediment properties

	SD	NB	CW	Units
Sediment moisture content	56	49	26	%
Cation exchange capacity[a]	52.9	54.9	25.2	meq 100 g^{-1}[b]
Organic matter[c]	5.64	5.48	1.54	%
Organic carbon	3.27	3.18	0.89	%
pH	8.22	7.42	7.42	

[a] Not corrected for calcium and magnesium extracted as free carbonates or gypsum

[b] Milliequivalent of hydrogen per 100 g

[c] Calculated by loss on ignition. Organic carbon calculated as 58 % of organic matter

dry weight equivalent) and 20 ml of a 0.01 M $CaCl_2$ aqueous solution were added to each jar to mimic submerged wetland conditions. After sample preparation, aerobic samples were allowed to re-equilibrate, uncovered, for 3 days at room temperature before the addition of 500 ng (250 μl of 2 mg l^{-1} methanol/water, 1:1, *v*/*v*) of each compound. The spiked samples were gently vortexed and then kept uncovered at room temperature. The samples were examined for signs of reduced layers in the sediment profile every other day. The water volume was also checked by weighing and deionized water was added to compensate for losses. After each water addition, samples were gently vortexed to ensure aerobic conditions throughout the experiment.

A similar microcosm setup as that in Lin et al. (2008) was used for the anaerobic degradation experiment. Aliquots of 10 g (dry weight equivalent) field wet sediment were weighed into 40-ml amber glass jars and 20 ml of a 0.01 M $CaCl_2$ aqueous solution were added to each sample. Uncovered sample vials were transferred into an airtight inflatable plastic glove chamber (Cole Parmer, Vermon Hill, IL, USA), flushed with nitrogen by alternately inflating and deflating the glove chamber, and equilibrated in the inflated glove chamber for 1 day, followed by sealing with screw caps with Teflon-lined butyl rubber septa. The samples were incubated in nitrogen for 12 days to ensure reduced conditions prior to addition of PPCPs. Sealed samples were then removed from the glove chamber and injected with 500 ng (50 μl of 10 mg l^{-1} methanol/water, 1:3, *v*/*v*) of each compound. Spiked samples were vortexed for 30 s and returned to the nitrogen-filled chamber for incubation at room temperature. The anaerobic conditions inside the vials were maintained by adding nitrogen into the plastic glove when noticeable deflation occurred.

A sterilized treatment was similarly prepared using the NB sediment in a solution identical to the nonsterilized treatment, but was amended with 100 ppm sodium azide to suppress the microbial activity. The sterilized treatment was included in both the aerobic and anaerobic experiments. The sterilized control was used to evaluate the contribution of biotic transformations to the overall degradation of the selected compounds in the sediments. Subsets of samples were sacrificed at each incubation interval (1, 3, 7, 14, 28, 56 and 112 days), and the entire soil and water contents were extracted and analyzed as described below.

2.4 Phase separation and sample extraction

To understand the phase distribution of PPCPs as a function of time, the sediment and water phases of each sample were analyzed separately when the samples were sacrificed for degradation measurement. The entire sediment and water from each sample was transferred to 50-ml glass centrifuge tubes and centrifuged at 3,400×*g* for 30 min to separate the solid and water phases. The supernatant was transferred to a 250-ml Erlenmeyer flask. Prior to PPCP extraction, the separated water and sediment phases were each spiked with deuterium labeled PPCPs as internal standards at 10 (ESI+) to 25 ng (ESI−) per sample. The sediment samples were extracted using a method similar to that of EPA Method 1694 (USEPA 2007) by mixing with 35 ml of phosphate buffer solution/methanol (3/4, *v*/*v*; pH 2.0) on a shaker for 60 min. The slurry was centrifuged at 3,400×*g* for 7 min and the supernatant was filtered through a Whatman No. 41 filter paper (Whatman, Maidstone, UK). The same extraction step was repeated two more times with 35 ml of 3/4 (*v*/*v*) pH 2.0 phosphate buffer solution/methanol and 20 ml methanol, respectively. The combined extracts were concentrated to about 30 ml on a vacuumed rotary evaporator at 60°C and diluted by addition of 250 ml reagent water prior to PPCP extraction.

The aqueous sample extraction and cleanup procedure was similar to the method described in Vanderford and Snyder (2006). Water or sediment extracts were passed through a preconditioned 6-ml (150 mg) oasis hydrophilic–lipophilic balance solid-phase extraction (SPE) cartridge (Waters, Millford, MA, USA). The SPE cartridges were preconditioned by passing through 5 ml methyl tert-butyl ether, 5 ml methanol, and 5 ml reagent water. The diluted aqueous samples were loaded onto the SPE cartridge at 10 ml min^{-1} using a Supelco vacuum manifold (Bellefonte, PA, USA), after which the cartridges were rinsed with 5 ml reagent water and then dried with a stream of nitrogen for 30 min. The cartridges were eluted with 5 ml methanol followed by 5 ml of 10/90 (*v*/*v*) methanol/methyl *tert*-butyl ether (MTBE) mixture. The resulting eluent was further condensed to <0.5 ml under a gentle stream of nitrogen. The extract was reconstituted to 1.0 ml with methanol–water (50:50, *v*/*v*) for analysis.

2.5 Sample analysis

Analysis of PPCPs was carried out on an Aquity ultraperformance liquid chromatography system coupled with a Trinity

triple quadrupole tandem mass spectrometer (LC-MS/MS) equipped with an electrospray ionization source (Waters, Milford, MA, USA). The separation was achieved using a BEH C18 column (100×2.1 mm i.d. with 1.7 μm particle size; Waters, Milford, MA, USA). Individual tune files were created by infusing the individual compounds to determine the optimum capillary and cone voltages, collision energies, and product ions. The MS/MS parameters, precursor, and product ions are listed in Table S1 in the Electronic supplementary material (ESM). The instrument detection limits ranged from 0.2 to 5 ng ml^{-1} for the different analytes over the length of the study. Recoveries and reproducibility of the selected PPCPs from water or sediment samples may be found in a previous study (Lin and Gan 2011; Lin et al. 2011).

2.6 Calculations

The phase distribution of each compound at each sampling interval was measured after separating the sediment and water phases. The apparent K_d' was calculated by dividing the concentration of a PPCP in sediment (C_s) over that in water (C_w), as is normally done when measuring the equilibrium sorption coefficient (K_d). However, K_d' differs from K_d in that K_d is determined at phase equilibrium after vigorous agitation usually for 24 h. Correlations and differences between the K_d' values were examined using R v2.14.1 (R Foundation).

To determine the half-life of each compound, the combined amounts (sediment and water) of each PPCP remaining at each sampling time point were fitted to an exponential decay model to estimate the first-order degradation rate constant k (per day), from which the $t_{1/2}$ was estimated. The half-life standard error was calculated using the standard error of the exponential decay model.Differences between the first-order rate constants of aerobic treatments, anaerobic treatments (when a half-life could be determined) and their corresponding sterilized soil samples were compared using R.

3 Results

3.1 Sediment properties

In general, the SD and NB sediments were similar with regard to cation exchange capacity (52.9 and 54.9 meq 100 g^{-1}, respectively) and organic carbon contents (3.27 and 3.18 %, respectively). In comparison, the CW sediment had much lower cation exchange capacity (25.2 meq 100 g^{-1}) and organic carbon content (0.89 %). The pH of both the NB and CW sediments was 7.42, while the SD sediment was slightly higher at 8.22 (see Table 1). The pH of the aqueous phase of the samples was nearly identical in samples spiked with PPCPs to those without PPCPs. However, there was a slight increase of about 1 pH unit, from 6.5 to 7.5 or 7.2 to 8.2, depending on the sediment type, in the aqueous pH of the aerobic samples over the first 28–56 days of incubation. This increase was not observed with the anaerobic samples, where the aqueous pH was relatively constant at about 7.2 for all three sediments (ESM Fig S1).

3.2 Phase distribution of PPCPs

In many of the sediment–PPCP combinations, K_d' consistently increased with increasing contact time, suggesting a lack of equilibrium or that aging increased PPCP sorption. Correlation analysis and Pearson's test at α=0.05 showed that in all DEET and carbamazepine treatments, including the sterilized treatments, K_d' values were positively correlated with incubation time. In addition, the correlation between K_d' and contact time was also significantly positive for ibuprofen in SD and NB under aerobic conditions, and for gemfibrozil in all treatments except the aerobic CW and the anaerobic sterilized treatments. The increasing trend of K_d' was also evident by comparing the K_d' values from day 112 (or the last measurable K_d' value) with day 1 (or the first time interval with a measurable K_d' value). Generally, the average K_d' of all compounds increased by factors of two to five under anaerobic conditions and by factors of two to 12 for aerobic treatments, while K_d' values for DEET under aerobic non-sterile conditions increased by factors of 23–34 (Tables 2 and 3). As the sorbed concentration, C_s was directly measured (rather than inferred by using sediment-less controls), the potential influence of microbial degradation on K_d' was eliminated. Therefore, the increases in K_d' over time suggested an aging effect, or that sorption of PPCPs to wetland sediments closely depend on the water retention time.

Of the four PPCPs, the apparent K_d' values were consistently the smallest for ibuprofen and the largest for carbamazepine, while gemfibrozil and DEET showed similar sorption potentials. In several instances for ibuprofen, calculation of K_d' was not possible due to rapid degradation, preventing statistical comparison between days 1 and 112 samples. It also appeared that for the same compound, the influence of sediment types, if any, was not statistically discernible. It is interesting to note that for DEET, significant increases in K_d' were observed for the aerobic treatments, while the increases for the anaerobic treatments were much more limited. For the aerobic sediments, the increases in K_d' were also considerably smaller for the sterilized sediment than for the nonsterilized sediments, suggesting that microbial activity may have contributed to the observed K_d' increases.

Table 2 Apparent phase distribution coefficient K_d' values for each compound and sediment under aerobic conditions

	Aerobic			
	DEET			
Day	SD	NB	CW	NB (sterile)
1	0.91±0.09	0.86±0.19	0.81±0.01	0.79±0.04
3	2.23±0.19	1.55±0.11	1.19±0.24	0.43±0.04
7	1.81±0.24	1.53±0.06	1.33±0.10	1.35±0.05
14	2.28±0.15	1.46±0.12	1.45±0.24	1.53±0.14
28	2.51±0.11	1.78±0.14	1.03±0.89	1.40±0.10
56	19.01±5.37	1.96±0.31	35.16±18.70	1.37±0.16
112	30.62±20.73	19.95±10.29	20.94±4.49	1.97±0.15
	Carbamazepine			
1	5.94±0.32	6.64±0.68	3.94±0.06	6.04±0.20
3	9.93±0.86	8.71±0.29	6.45±0.66	6.13±0.30
7	8.46±0.42	8.73±0.74	8.34±0.38	9.07±0.38
14	10.01±0.34	7.32±0.56	8.64±1.15	9.07±0.55
28	10.94±0.41	8.94±0.45	8.77±0.44	8.55±0.33
56	11.80±0.72	9.13±0.52	10.96±0.93	8.70±0.47
112	12.78±0.77	10.48±1.08	15.11±2.12	9.45±0.78
	Ibuprofen			
1	–[a]	0.68±0.15	0.30±0.01	0.28±0.07
3	0.55±0.49	0.89±0.07	0.45±0.16	–
7	–	0.17±0.01	0.32±0.04	0.70±0.07
14	0.08±0.12	0.60±0.27	0.36±0.07	0.67±0.03
28	0.24±0.19	0.58±0.09	0.29±0.04	0.62±0.08
56	2.47±1.23	2.62±1.73	–	0.89±0.71
112	–	–	–	0.88±0.57
	Gemfibrozil			
1	0.77±0.10	1.84±0.37	1.17±0.04	1.63±0.10
3	0.26±0.04	2.27±0.20	1.65±0.14	1.48±0.10
7	0.80±0.06	0.29±0.01	1.73±0.07	2.65±0.18
14	1.20±0.19	1.59±0.17	1.52±0.22	2.58±0.28
28	0.90±0.10	1.68±0.19	1.55±0.04	2.45±0.18
56	2.10±0.53	7.80±3.37	–	3.52±0.36
112	8.20±2.08	–	–	20.11±9.09

[a] Indicates that concentration in either the soil or water was insufficient to calculate K_d' value

Table 3 Apparent phase distribution coefficient K_d' values for each compound and sediment under anaerobic conditions

	Anaerobic			
	DEET			
Day	SD	NB	CW	NB (sterile)
1	0.70±0.41	1.10±0.13	0.54±0.08	1.01±0.02
3	1.01±0.58	0.89±0.29	0.83±0.11	–[a]
7	1.93±0.25	1.52±0.12	1.14±0.04	1.40±0.05
14	1.22±0.05	1.29±0.04	1.22±0.26	1.26±0.03
28	1.69±0.15	1.54±0.02	1.65±0.16	1.32±0.05
56	2.07±0.27	1.38±0.55	1.73±0.47	1.13±0.34
112	2.08±0.07	1.90±0.12	1.78±0.21	1.68±0.10
	Carbamazepine			
1	3.94±1.36	5.82±0.43	2.93±0.44	5.91±0.44
3	5.05±2.34	5.28±1.00	3.59±0.36	–
7	7.59±1.23	7.15±0.31	4.41±0.17	6.89±0.28
14	6.45±0.34	7.30±0.69	5.38±0.93	6.63±0.38
28	1.05±0.17	8.44±0.25	7.07±0.68	7.15±0.24
56	9.80±0.54	8.39±1.31	8.86±1.44	6.71±1.06
112	10.55±0.32	10.86±0.46	10.19±0.78	8.95±0.38
	Ibuprofen			
1	–	0.45±0.13	0.07±0.03	0.36±0.08
3	–	0.21±0.16	0.19±0.05	–
7	0.38±0.07	0.79±0.15	0.20±0.05	0.48±0.03
14	0.12±0.09	0.51±0.08	0.32±0.09	0.44±0.09
28	0.37±0.28	0.68±0.12	0.44±0.07	0.48±0.08
56	0.46±0.04	0.54±0.39	0.33±0.11	0.29±0.07
112	0.24±0.14	0.75±0.08	0.16±0.13	0.45±0.18
	Gemfibrozil			
1	0.50±0.39	1.44±0.25	0.63±0.15	1.68±0.26
3	0.68±0.43	1.37±0.48	0.85±0.16	–
7	1.60±0.24	1.86±0.19	0.94±0.08	1.69±0.24
14	1.35±0.12	1.82±0.17	1.36±0.22	1.76±0.15
28	2.06±0.14	2.25±0.13	1.52±0.50	1.86±0.16
56	2.63±0.31	1.82±0.97	2.02±0.39	1.53±0.35
112	2.42±0.22	2.42±0.23	2.01±0.42	1.86±0.08

[a] Indicates that concentration in either the soil or water was insufficient to calculate K_d' value

3.3 Half-lives of PPCPs

In aerobic samples, the concentrations of DEET, ibuprofen, and gemfibrozil decreased rapidly and <20 % of each compound remained after 56 days (Fig. 1). Aerobic dissipation was less pronounced for carbamazepine and greater than half of the original concentration remained at the end of incubation. Under anaerobic conditions, all PPCPs became more persistent, and no compound decreased to <50 % of the spiked amount at the end of incubation, with carbamazepine in the San Diego creek sediment as the only exception (Fig. 2). Additionally, the use of sodium azide to suppress microbial activity in the sediment appeared to be only partially effective. This is demonstrated in Figs. 1 and 2, where sterile samples showed similar trends to the other treatments. In aerobic sediments containing DEET and gemfibrozil, degradation was significantly inhibited ($p<0.001$) after sterilization, suggesting a role of microorganisms in the transformation of these PPCPs in sediments.

The dissipation of all four compounds under aerobic conditions was successfully fitted ($R^2=0.72–0.98$) to the

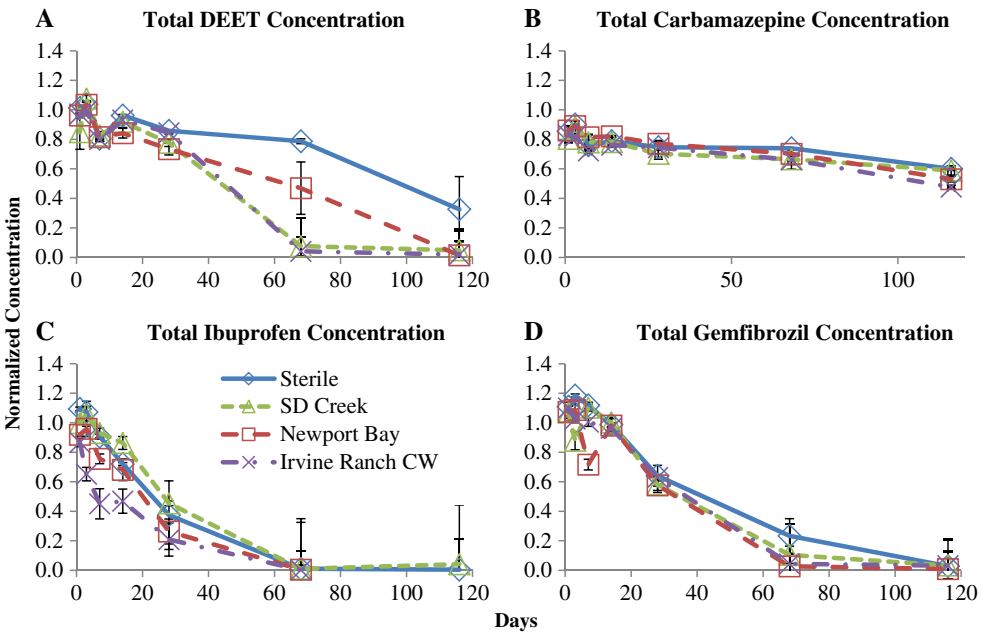

Fig. 1 Change in the total (sum of the soil and water concentrations) normalized aerobic concentrations of **a** DEET, **b** carbamazepine, **c** ibuprofen, and **d** gemfibrozil throughout the duration of incubation. Error bars represent standard error

exponential decay model, while the fit of data from the anaerobic experiment was weaker (R^2=0.00–0.81). The reduced quality of model fit was the result of slow degradation. For example, the degradation of all PPCPs in the anaerobic sediments was so slow that the extrapolated half-lives were consistently longer than the actual incubation duration (112 days).

For the same PPCP, more rapid degradation occurred under aerobic conditions as compared to anaerobic conditions (Tables 4 and 5). Carbamazepine consistently had the longest half-lives (165±13.33–264±35.81 days) under aerobic conditions, while the half-lives of ibuprofen (7±0.85–19±3.11 days) and gemfibrozil (15±0.78–22±0.83 days) were much shorter. The half-life of DEET was 18±1.25–24±1.78 days in the nonsterilized soils, while it increased to 81±10.86 days after sterilization, suggesting an important role of microbial transformations. The half-lives for anaerobic samples increased to 228±57.54–782±539.72 and 207±33.71–546±166.75 days for gemfibrozil and ibuprofen, respectively, in the NB, CW, and sterilized control sediments. It was not possible to estimate the half-life of DEET in all sediments or ibuprofen and gemfibrozil in the SD sediment because of a lack of appreciable degradation. Carbamazepine had the smallest change in persistence between aerobic and anaerobic conditions, with a 1.5–2.5

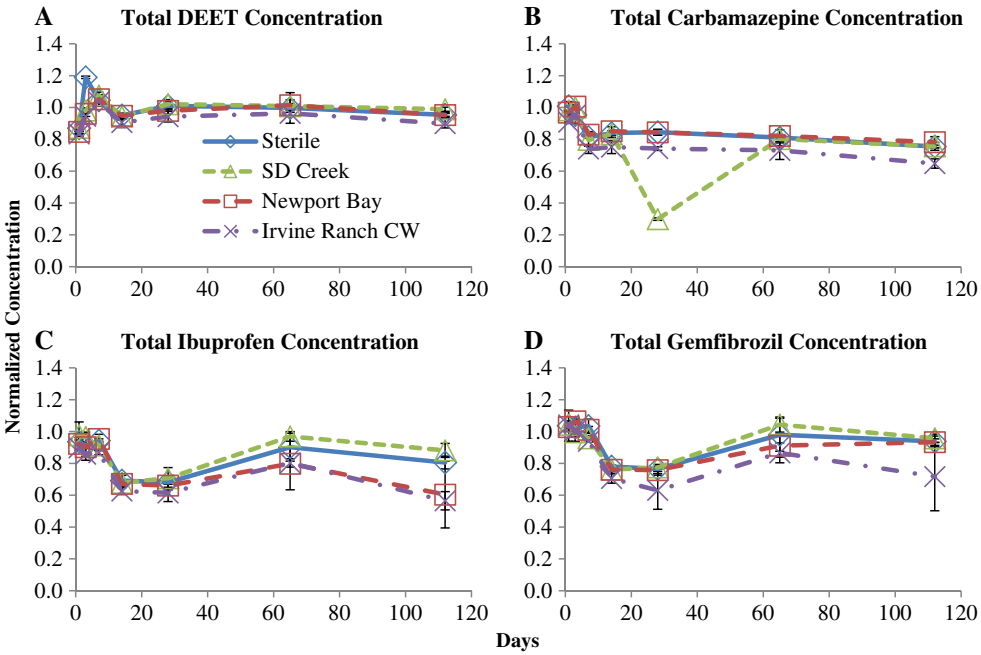

Fig. 2 Change in the total (sum of the soil and water concentrations) normalized anaerobic concentrations of **a** DEET, **b** carbamazepine, **c** ibuprofen, and **d** gemfibrozil throughout the duration of incubation. Error bars represent standard error

Table 4 Degradation rate constant (k) and half-lives ($t_{1/2}$) with standard error of the test compounds under aerobic conditions

	SD Creek			Newport Bay			Irvine Ranch CW			Sterile (Newport Bay)		
	k (day^{-1})	$t_{1/2}$ (day)	r^2	k (day^{-1})	$t_{1/2}$ (day)	r^2	k (day^{-1})	$t_{1/2}$ (day)	r^2	k (day^{-1})	$t_{1/2}$ (day)	r^2
DEET	0.0294	24±1.78	0.91	0.0328	21±2.33	0.84	0.0382	18±1.25	0.93	0.0086	81±10.86	0.80
CBZ	0.0030	235±28.27	0.82	0.0040	172±9.70	0.95	0.0042	165±13.33	0.91	0.0026	264±35.81	0.80
IBU	0.0372	19±3.11	0.72	0.0812	9±0.44	0.96	0.0946	7±0.85	0.85	0.0539	13±0.80	0.94
GEM	0.0322	22±0.80	0.97	0.0457	15±0.78	0.95	0.0351	20±1.76	0.89	0.0318	22±0.83	0.98

times (281±74.73–439±136.73 days) increase depending on the sediment type. Gemfibrozil (11–34×), DEET (static), and ibuprofen (24–27 times), however, all exhibited large increases in their half-lives under anaerobic conditions, particularly in the SD sediment.

4 Discussion

4.1 Sorption

The apparent sorption coefficient K_d' consistently increased over the course of the experiment for DEET, carbamazepine, and gemfibrozil in both aerobic and anaerobic sediments (see Tables 2 and 3). The analysis of PPCPs in the water phase showed that the aqueous concentration generally decreased at a faster rate than the sediment concentration. This may be attributed to continuous sorption to the sediment phase caused by the lack of equilibrium, preferential transformations of PPCPs in the aqueous phase over the sediment phase (Tappe et al. 2008) or both. For instance, in the biologically active reduced sediments, DEET did not degrade appreciably. The amount of DEET in the water phase decreased by ~2 ng day^{-1} during the incubation, while the fraction in the sediment phase roughly increased at the same rate. Continuous partitioning of DEET into the sediment phase in the absence of a diffusion gradient caused by degradation implied that a longer contact time would increase sorption to wetland sediments.

Previous research suggests that the increased sorption of organic compounds in soils or sediments is due to the effect of "aging" (Alexander 2000). It is commonly believed that as contact time increases, compounds diffuse to less accessible sorption sites, making them less likely to desorb. Aging coupled with uneven degradation of the compound in the aqueous and sorbed phases was previously found to contribute to a shift to the sediment phase in the partitioning of pesticides as a function of contact time (Bondarenko and Gan 2004).

Carbamazepine and DEET are moderately hydrophobic (log K_{ow} 2.25 and 2.18, respectively) compounds that are neutral at environmentally relevant pH. Carbamazepine displayed the highest sorption potential among the four PPCPs considered in this study. Previously published K_d' values for carbamazepine are 1.43 (0.24 % OC), 1.7 (0.74 % OC) and 12.3 (4.36 % OC; Scheytt et al. 2005; Stein et al. 2008), indicating that the OC content of soils or sediments plays a role in carbamazepine sorption. The higher K_d' of 12.3 lkg^{-1} observed for the 4.36 % OC sediment is similar to the range (9–15 lkg^{-1}) observed at day 112 for sediments with similar OC content in this study. However, an analysis of the influence of sediment OC content on K_d' of carbamazepine did not show a significant correlation in this study. In both the aerobic and anaerobic experiments, carbamazepine sorption was significantly greater in the SD (3.81 % OC) and CW (0.89 % OC) sediments as compared to the NB sediment (only aerobic) or sterilized NB sediment, even though the NB sediment had 3.81 % OC content. Likewise, there was also

Table 5 Degradation $t_{1/2}$ with standard error of the test compounds under anaerobic conditions

	SD Creek			Newport Bay			Irvine Ranch CW			Sterile (Newport Bay)		
	k (day^{-1})	$t_{1/2}$ (day)	r^2	k (day^{-1})	$t_{1/2}$ (day)	r^2	k (day^{-1})	$t_{1/2}$ (day)	r^2	k (day^{-1})	$t_{1/2}$ (day)	r^2
DEET	–[a]	S[b]	–	–	S	–	–	S	–	–	S	–
CBZ	0.0018	382±138.11	0.47	0.0016	439±136.73	0.48	0.0025	281±74.73	0.54	0.0017	408±121.14	0.49
IBU	–	S	–	0.0032	220±91.54	0.38	0.0034	207±33.71	0.81	0.0013	546±166.75	0.60
GEM	–	S	–	0.0011	603±189.27	0.57	0.0030	228±57.54	0.65	0.0009	782±539.72	0.38

[a] Values were not determined due to lack of measurable degradation

[b] Indicates that concentrations were static throughout the incubation

no discernible response of the apparent sorption of DEET to the sediment OC content. The results indicate that while carbamazepine and DEET are present in a nondissociated form at the environmental pH, organic carbon is not the only factor influencing their sorption. It is likely that other variables, such as cation exchange capacity, concurrently affect the phase partition of such PPCPs in a sediment–water binary system.

Gemfibrozil and ibuprofen are both polar compounds that are present as anions under environmentally relevant pH conditions. Previous studies show that gemfibrozil and ibuprofen have low sorption to mineral sediments with K_d' of 0.8 and 0.7 lkg^{-1}, respectively (Lin et al. 2006). These values are in good agreement with our results for ibuprofen and gemfibrozil. Due to their negative charge, it is unlikely that the negatively charged mineral surfaces in the sediments played a significant role in the sorption of gemfibrozil or ibuprofen. Low sorption of ibuprofen and gemfibrozil to the sediment likely contributed to their relatively rapid degradation in the aerobic sediments, as weak sorption would result in better availability of the compound to the degrading microorganisms.

Sorption of organic compounds in soils or sediments is generally correlated with soil/sediment OC content. However, the sorption of the four selected PPCPs could not be explained by sediment OC content alone. This observation reaffirms that PPCPs are more complex than traditional nonpolar organic compounds, as PPCPs can be weak acids, weak bases, or zwitterions (Brooks et al. 2009), and that their sorption in sediments cannot be simply predicted from the sediment OC content. Given the wide range of structures of PPCPs, many mechanisms (e.g., hydrogen bonding, surface complexation, and cation bridging) may be involved in sorption of PPCPs (Brooks et al. 2009) and must be characterized individually.

4.2 Persistence under aerobic and anaerobic conditions

Degradation of the selected PPCPs was generally inhibited under reduced conditions as compared to aerobic experimental conditions. Previous research comparing aerobic to anaerobic half-life values of PPCPs in environmental samples is sparse, with most half-life values (if available at all) only being determined under aerobic conditions, much less in the context of wetland sediments (Kunkel and Radke 2008; Benotti and Brownawell 2009; Yamamoto et al. 2009). The experimental design prevented accurate measurement of redox potential due to the small container size and the potential to introduce oxygen into the reduced samples. However, due to the extended incubation (112 days) under N_2, it can be assumed that the anaerobic samples became highly reduced (as was also indicated by the sulfur odor and release of gas when opening sample vials). Aerobic sediments mimic sediment layers at the sediment–water interface of a well-mixed or aerated system, while the anaerobic sediments represent either a poorly mixed slow moving wetland or sediment below the oxic layer.

While appreciable degradation occurred in the aerobic sediments, DEET was so persistent under anaerobic conditions that calculation of a meaningful half-life was impossible for any of the sediments. A lack of detectable degradation under anaerobic conditions indicates that DEET will persist if present in anaerobic regions of wetlands, such as in subsurface sediments or in areas with stagnant flow. While the use of sodium azide was not effective at completely sterilizing the sediment throughout the incubation, the half-life of DEET in the aerobic soils with the sodium azide amendment was significantly ($p<0.001$) longer than that in the nonsterile soils, indicating a contribution of microbial transformations. No previous information is available for comparing DEET persistence under different soil or sediment conditions. Carbamazepine is one of the most commonly detected PPCPs in the environment and its frequent detection is attributed to its recalcitrance to degradation (Conkle et al. 2008; Benotti and Brownawell 2009; Patterson et al. 2010; Yu and Wu 2011). Previously published aerobic half-life values of carbamazepine range from 88 to 495 days, which coincide with the half-life values obtained in this study (Benotti and Brownawell 2009; Yamamoto et al. 2009; Patterson et al. 2010; Walters et al. 2010). The anaerobic half-life values found in this study are near the high end (495 days) of the previously reported half-life values for carbamazepine under aerobic conditions (Walters et al. 2010). The increases (1.5–2.6 times) in persistence for carbamazepine under anaerobic conditions were relatively less than that for the other compounds. The half-lives for carbamazepine under either aerobic or anaerobic conditions indicate that carbamazepine is relatively persistent in wetland sediments, as previously observed for other environmental matrices such as biosolids, estuarine waters, and aquifers.

Under aerobic conditions, gemfibrozil displayed a relatively short persistence with half-lives of 15–22 days, which was in the low range (10.5–289 days) of the reported half-life values in the literature (Kunkel and Radke 2008; Walters et al. 2010; Araujo et al. 2011). However, the persistence of gemfibrozil in the same sediments under anaerobic conditions drastically increased, with half-lives ranging from >7 months to interminable (see Table 5). The anaerobic half-life values of gemfibrozil were up to 2.5 times larger than the high values reported for aerobic soils or in water (Walters et al. 2010; Araujo et al. 2011). Kunkel and Radke (2008) and Lin et al. (2011) evaluated gemfibrozil degradation in reduced soils and also found essentially no degradation after 8 and 84 days of incubation, respectively. No other data for the degradation of

gemfibrozil under anaerobic conditions are available in the literature. Of the selected PPCPs, ibuprofen appeared to be the least persistent under aerobic conditions with half-lives of 7–19 days in the nonsterilized sediments. Our observed half-lives were also comparable to the values (18–19 days) reported by Yamamoto et al. (2009) in aquatic environments. However, degradation of ibuprofen was greatly inhibited under anaerobic conditions and the half-lives were prolonged to about 7 months to indeterminable, suggesting again that even readily degradable PPCPs may persist for a long time in reduced sediments.

5 Conclusions and implications for wetland treatment

As water containing suspended particles and dissolved contaminants passes through a wetland, the contaminants may be physically retained and hence removed from the water flow as the suspended particles settle under gravity or become trapped (e.g., by vegetation) or the dissolved chemicals are sorbed to the bed sediment via phase partitioning. Given the low to moderate sorption potentials for most PPCPs, the fraction attached to suspended particles and its subsequent retention may be negligible, which makes partitioning from the water phase to the bed sediment an important pathway for removal. Results from this study show that sorption to the sediment phase varied among the different PPCPs. Therefore, when wastewater passes through a wetland system, PPCPs may be retained at different rates as dictated by the sorption potentials. Our results indicate that for PPCPs such as carbamazepine and DEET, their removal by wetland sediment may be more pronounced than that for ibuprofen or gemfibrozil. In addition, as shown in this study, the actual phase distribution increases with contact time, suggesting that a long hydrologic residence time would be essential for maximizing the retention of PPCPs by wetland sediments. Furthermore, K_d derived from batch equilibrium measurements may result in overestimations of the efficacy of treatment wetlands with short retention times (hours or days) in the removal of PPCPs, since equilibrium of the compound between sediment and water may not be reached.

In wetlands, the sediment floor generally consists of aerobic zones near the sediment surface with rapidly decreasing oxygen levels as the sediment depth increases. However, this decrease in oxygen is not uniform with depth. Wetland sediment heterogeneity results in microsites with different redox potentials (Rabenhorst et al. 2010). The drastic differences in the persistence of PPCPs between aerobic and anaerobic conditions, as observed in this study, suggest that variations in wetland redox potential likely plays an important role in determining the degradation of PPCPs following the retention of PPCPs by the wetland (White et al. 2006). As PPCPs become buried in the bed sediment, the expected reduced conditions in the subsurface layers may substantially prolong the persistence of the imbedded compounds. When constructing a treatment wetland or modifying an existing wetland for wastewater treatment purposes, the aerobic nature of the water and sediment column is vital to the treatment efficiency for PPCPs. To achieve more rapid degradation of PPCPs, aeration below the sediment–water interface may be desired. If using a natural wetland, treatment for PPCPs would be optimized by ensuring that water entering the wetland is saturated with oxygen to prevent anaerobic zones near the sediment–water interface. In addition, the use of a subsurface flow treatment wetland would be more efficient if oxygen levels can be sufficiently maintained throughout the wetland treatment zone.

The lack of degradation under reduced conditions also implies that once present in the subsurface of a wetland floor, PPCPs may persist for a prolonged time. While sediment burial may be an effective means for the removal of PPCPs from treated wastewater, there exists the risk that disturbances to the wetland floor, such as large rain events and clean-up or reconstruction of the wetland, may lead to a pulsed, albeit delayed, release of the accumulated PPCPs due to desorption (Conkle et al. 2010). Therefore, the long-term persistence of PPCPs in wetland sediments and the risk for their potential release back into the open environment merits consideration and, in particular, evaluation under field conditions.

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