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Degradation of Emerging Organic Contaminants in an Agricultural Soil: Decoupling Biotic and Abiotic Processes

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Abstract Although there is a growing interest in emerging organic contaminants (EOCs), most research is focused on wastewater treatment, the occurrence of EOCs, and their fate in the aquatic environment. There is limited information about their behavior in agricultural soils, where they can be introduced via irrigation with treated wastewater (TWW). In this study, the degradation in an agricultural soil of eight EOCs (bisphenol A, carbamazepine, diethyl phthalate, ethyl paraben, 5-methyl-1*H*-benzotriazole, primidone, Surfynol 104, and tris(2-chloroethyl) phosphate) with a broad range of physical-chemical properties was monitored for 40 days. Two types of soil treatments were performed: non-sterilization and sterilization. In the non-sterilized soil, by the end of the incubation period, degradation was greater than 70% for all the target compounds except carbamazepine, Surfynol 104, and primidone (<50%). In contrast, in the sterilized soil, the degradation of most of the compounds was less than 50%, except ethyl paraben, 5-methyl-1*H*-benzotriazole, and diethyl phthalate (>70%). These findings indicate that soil sterilization reduces overall degradation rates, which suggests that microbial activity plays an important role in the degradation of most of the EOCs studied in soil.

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1 Introduction

Emerging organic contaminants (EOCs) have been detected in the aquatic environment, mainly because of anthropogenic activities (Bell et al. 2011; Petrie et al. 2015). Among them, pharmaceutical and personal care products (PPCPs), endocrine disruptors, and biocides are the contaminants of greatest environmental and health concern. As treated wastewater (TWW) treatment plants are not designed to remove these contaminants efficiently (Luo et al. 2014), research has mainly focused on aquatic systems (Lapworth et al. 2012; Li 2014). Although these EOCs have also been detected in other environmental compartments such as soils (Li 2014), the processes affecting their fate are less understood.

In arid and semiarid countries, TWW is used in agricultural irrigation due to water scarcity (United Nations 2014). Moreover, sludge is often added to agricultural soils to improve soil quality. Although sludge is known to contain many contaminants that can interact with the soil, their occurrence in soil or sludge is not regulated.

Therefore, once these EOCs reach the soil, depending on their physical-chemical properties, several processes can occur, such as sorption, transport to aquifer or surface waters, degradation, or uptake by plants (Gibson et al. 2010; Avisar et al. 2009). Consequently, it is

important to study the processes involved in the dissipation of EOCs and to assess the bioavailable-bioaccessible fraction of the EOCs in soil.

Moreover, degradation is one of the most important dissipation processes for these EOCs. It can include hydrolysis, photolysis, or biodegradation. In soil, the microbiota consists mostly of fungi and bacteria that decompose organic matter, releasing nitrogen, which is necessary for plants. However, this microbial biomass can also degrade organic compounds. Therefore, biodegradation and biotransformation play an important role in the fate of EOCs.

Despite its suspected relevance, few studies have focused on the biodegradation of EOCs in agricultural soils. Instead, most have assessed EOC attenuation, due to the difficulty of distinguishing degradation from biodegradation. The main objective of this study was to assess the biodegradation kinetics of a mixture of different EOCs in a representative agricultural soil. To achieve this, a sterilization treatment was performed on the soil to minimize the microbial activity in the control samples. EOC concentrations were then monitored for 40 days. The research hypothesis was that overall degradation of EOCs would be lower in soil under a sterilization treatment than in the same soil when it had not been sterilized.

2 Materials and Methods

2.1 Reagents and Contaminants

Bisphenol A (BPA, 99%), carbamazepine (CBZ, 99%), ethyl paraben (EP, 99%), 5-methyl-1*H*-benzotriazole (5-TTri, 98%), primidone (PMD, 99%), Surfynol 104 (S104, 98%), and tris(2-chloroethyl) phosphate (TCP, 97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Diethyl phthalate (DEP, 99%) was purchased from Riedel-de Haën (Seelze, Germany). The physical-chemical properties of the selected contaminants are listed in Table 1.

The internal standard triphenylamine (TPhA) and the derivatization reagent trimethylsulfonium hydroxide (TMSH) were purchased from Sigma-Aldrich. Ethyl acetate, methanol, SupraSolv®-quality hexane, and hydrochloric acid (37%) were purchased from Merck (Darmstadt, Germany).

2.2 Soil

The soil used was collected from the surface horizon of a Typic Xerorthents soil from the Llobregat River Delta's agricultural area (longitude 2° 03′ E, latitude 41° 17′ N). The soil had a sandy texture (90% sand, 8% silt, and 2% clay) with a pH of 8.1 (soil-to-water ratio 1:10) and soil electrical conductivity of 3.8 dS m^{-1} (soil-to-water ratio 1:10). Total organic carbon and total organic nitrogen content were 5 and 0.7 g kg^{-1}, respectively. The cation exchange capacity (CEC) was 3.8 meq 100 g^{-1}, and exchangeable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} were 2.82, 0.64, 0.25, and 0.15 meq 100 g^{-1} soil, respectively.

2.3 Biodegradation Assay

Biodegradation tests were performed using the procedure described in Xu et al. (2009). To assess the contribution of biodegradation, a subsample of the soil was sterilized. Therefore, two different treatments were applied to the soil, namely (i) sterilization and (ii) non-sterilization. Both were applied in triplicate. Briefly, the soil sterilization was performed in an autoclave at 120 °C and a pressure of 300 kPa for 45 min three times on three consecutive days.

In glass tubes, 5 g of both the sterilized and non-sterilized soils were spiked with a mixture of contaminants to achieve a soil concentration of 50 μg kg^{-1} of each contaminant. Then, MilliQ water was added to the tubes at 70% of soil water capacity (1.4 mL approximately). The tubes were kept from the light with aluminum foil and sealed with glass wool to ensure aerobic conditions. All the tubes were incubated at 23 ± 1 °C for 0, 0.25, 0.5, 1.3, 3, 7.2, 17, and 40 days. Experiments were conducted in triplicate, and blanks (soils without contaminants) and controls (contaminants without soils) were also included in the experiment.

2.4 Soil Extraction

The extraction of contaminants from the soil was adapted from the method described in Xu et al. (2009). Following incubation for different times, contaminants were extracted from the soils with 5 mL of acetone/hexane (1:1, *v*/*v*) through sonication for 15 min. The tubes were then centrifuged at 3100*g* for 10 min. The extraction was performed three times, and the extracts were combined and further evaporated with a nitrogen stream to a final volume of 0.5 mL. The final extract was

Table 1 Properties of the contaminants added obtained using EPISuite, U.S. Environmental Protection Agency (US EPA)

EOC	p*K*a values[a]	Solubility (mg L^{-1})	Neutral log K_{OW}	log K_{OA}	log K_{AW}	K_{OC} (L kg^{-1})	*fn*
Bisphenol A (BPA)	9.8[0/−] 10.4[−/2−]	120	3.64	12.75	−9.43	1245	0.974
Carbamazepine (CBZ)	NA	112	2.25	10.81	−8.36	168.6	1.000
Diethyl phthalate (DEP)	NA	1080	2.65	7.02	−4.60	135.70	1.000
Ethyl paraben (EPB)	8.5[0/−]	885	2.49	9.18	−6.71	246.9	0.666
5-Methyl-1*H*-benzotriazole (5-TTri)	0.77[+/0] 8.85 [0/−]	3069	1.71	6.89	−5.18	87.87	0.817
Primidone (PMD)	2.36[+/0] 3.94[0/−] 5.42[−/2-]	500	0.73	9.01	−8.10	23.84	0.003
Surfynol 104 (S104)	13.15[0/−] 13.83[−/2−]	26.35	3.61	8.61	−5.00	125.60	1.000
Tris(2-chloroethyl) phosphate (TCP)	NA	7000	1.63	5.31	−3.87	66.83	1.000

[0] neutral, [+] cationic, [−] anionic, *NA* not applicable, K_{OW} (L L^{-1}) the partition coefficient octanol to water for the neutral molecule, K_{OA} (L L^{-1}) the partition coefficient octanol to air, K_{AW} (L L^{-1}) the partition coefficient air to water for neutral molecules (known as dimensionless Henry's Law constant), K_{OC} (L kg^{-1}) the soil organic carbon-water partition coefficient, *fn* the neutral fraction at soil pH (8.1)

[a] Dissociation reaction

reconstituted with 100 mL of deionized water, and its pH was adjusted to between 2 and 3 with HCl. Afterwards, samples were percolated through SPE cartridges (Strata X, 100 mg 6 mL^{-1}) previously conditioned with 6 mL of hexane, ethyl acetate, methanol, and water, respectively. The cartridges were vacuum dried and eluted with 10 mL of ethyl acetate. The extracts were then concentrated to a final volume of 200 μL with a nitrogen stream, and TPhA was added as internal standard. Finally, a 50 μL aliquot was derivatized with 10 μL of TMSH. Samples were injected in a Bruker Scion SQ GC-MS. The experimental conditions are described in the Supplementary Information (SI).

2.5 Data Calculation

Concentrations of the different contaminants were plotted against time. All the data were adjusted to three different kinetics:

$$\text{Zero-order}: [A] = [A]_0 - kt \quad (1)$$

$$\text{First-order}: [A] = [A]_0 e^{-kt} \quad (2)$$

$$\text{Second-order}: 1/[A] = kt + 1/[A]_0 \quad (3)$$

where $[A]$ is the concentration of the contaminant at time t (day), $[A]_0$ is the initial concentration, and k is the degradation rate. Finally, half-life values of the contaminants in both soils were estimated based on the adjusted kinetics.

3 Results and Discussion

In this study, EOCs were selected with different physical-chemical properties (Table 1). Among these properties, hydrophobicity, solubility, and volatility play an important role in adsorption and soil dissipation processes. Hydrophobic compounds ($\log K_{OW} > 3$) such as BPA and S104 usually have higher K_d or K_{OC} values and are thus highly adsorbed into the soil compared to hydrophilic compounds. High K_d values lead to a reduction in the bioavailability of these contaminants to bacteria. Furthermore, the $\log K_{AW}$ and $\log K_{OA}$ indicate the tendency of contaminants to migrate from water or soil, respectively, to the atmosphere by volatilization. All the contaminants selected for this study except TCP will remain in soil or pore water. Accordingly, soil sorption, biodegradation, and hydrolysis for carboxylic acid esters (DEP, EPB, and TCP) are the most significant processes to remove them from pore water.

The EOC concentrations were determined for both soils for different incubation times up to 40 days. The resulting degradation curves are shown in Fig. 1. After 40 days of incubation, significant differences were

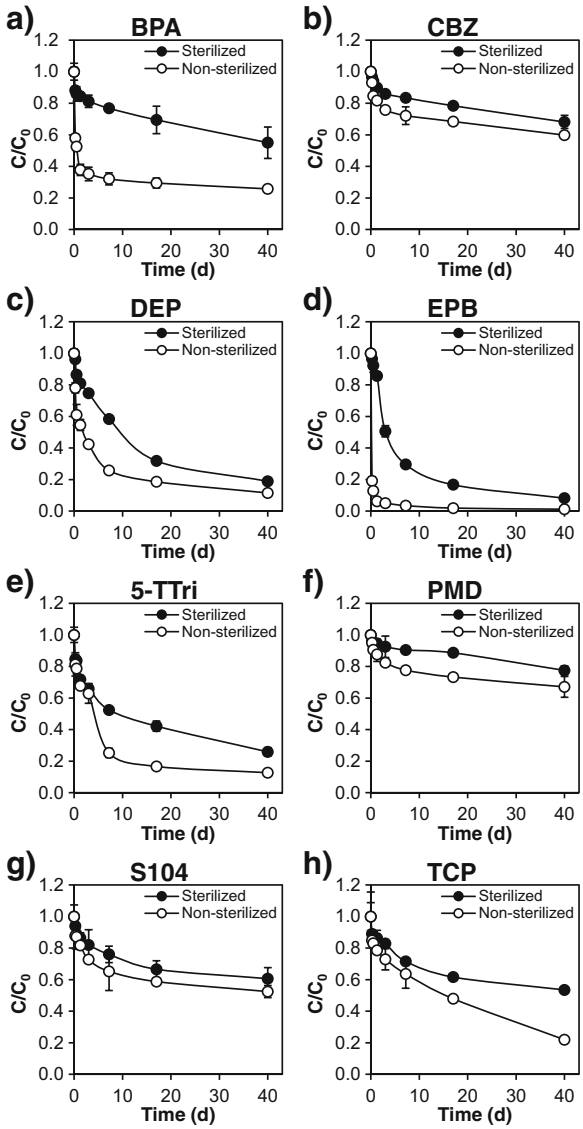

Fig. 1 Degradation curves for both sterilized (*black*) and non-sterilized (*white*) soils along the incubation time in days of the studied EOCs: BPA (**a**), CBZ (**b**), DEP (**c**), EPB (**d**), 5-TTri (**e**), PMD (**f**), S104 (**g**), and TCP (**h**)

found between the two treatments (non-sterilized and sterilized soil). For most of the EOCs, dissipation in non-sterilized soil was higher than in sterilized soil.

The degradation values for the different EOCs in each soil are shown in Table 2. For example, in non-sterilized soil, some EOCs (BPA, DEP, EPB, and 5-TTri) showed a degradation of over 70% at 7 days. Conversely, other EOCs (CBZ, PMD, and S104) showed a degradation of less than 50% of the initial concentration at 40 days. Furthermore, EPB exhibited the fastest degradation; after only 12 days, its degradation was greater than 80%. Similar behavior was observed for the sterilized soil, where EOCs such as BPA, CBZ, PMD, and S104 exhibited degradation of less than 50% after 40 days of incubation. In contrast, after the same incubation time, other EOCs (DEP, EPB, and 5-TTri) had degraded more than 70%.

Depending on the nature of the EOCs, other dissipation mechanisms such as sorption, volatilization, photolysis, or hydrolysis could occur. However, in this study, the tubes were covered with aluminum foil to minimize photolysis processes. Therefore, photodegradation was negligible, and sorption and hydrolysis seemed to be the other two most important degradation mechanisms. For this reason, the differences between the treatments could be mainly due to aerobic biodegradation, while degradation in the sterilized soil could be attributed to sorption or hydrolysis processes for DEP, EPB, and TCP.

Experimental values were fitted to three degradation kinetics (zero-, first-, and second-order) to estimate degradation rates (k) and half-life ($t_{1/2}$) values (Table 3) in order to obtain the best fit with experimental data.

For sterilized soil, correlations were slightly better when the experimental values were fitted to a second-order kinetics (R^2 from 0.783 to 0.992) than to the zero- and first-order kinetics (R^2 from 0.647 to 0.929 and 0.706 to 0.984, respectively). Half-life values ranged from 3.7 to >40 days.

Generally, for non-sterilized soil, correlations were worse than for sterilized soil. The second-order kinetics exhibited stronger correlations (R^2 from 0.716 to 0.986) than the zero- or first-order kinetics (R^2 from 0.481 to 0.720 and 0.661 to 0.896, respectively). Half-life values ranged from 0.7 to >40 days and were generally lower than in sterilized soils.

Usually, experimental values are fitted to first-order kinetics by default; however, as seen in Fig. 2, second-order kinetics fit the experimental values better. Consequently, the contaminants' half-lives can be accurately predicted.

This better fit for second-order has been showed by other authors. In these studies, the better adjustment was attributed to co-metabolism (Schwarzenbach et al. 2005). Although in sterilized soil, the amount of bacteria was minimized, they could grow during the experiment as tubes were under aerobic conditions. Moreover, other processes such as hydrolysis take place for some compounds, e.g. hydrolysis of ester (EPB).

Once again, the differences between treatments show that the sterilization treatment resulted in decreased

Table 2 Degradation (%) of the studied EOCs along the incubation time for both sterilized and non-sterilized soils (±SD, $N = 3$)

EOC	Soil	Time (day) 0.25	0.5	1.3	3	7.2	17	40
BPA								
	Sterilized	12 ± 2	14 ± 5	16 ± 1	19 ± 4	23 ± 1	31 ± 9	45 ± 10
	Non-sterilized	42 ± 2	48 ± 2	62 ± 4	65 ± 4	68 ± 4	71 ± 3	74 ± 2
CBZ								
	Sterilized	3.3 ± 1.2	5.8 ± 1.0	10 ± 1	14 ± 1	17 ± 1	22 ± 1	32 ± 4
	Non-sterilized	6.9 ± 2.2	15 ± 1	18 ± 1	24 ± 1	28 ± 6	32 ± 1	40 ± 1
DEP								
	Sterilized	3.8 ± 0.7	14 ± 2	19 ± 1	25 ± 1	42 ± 2	68 ± 1	81 ± 1
	Non-sterilized	22 ± 3	39 ± 7	45 ± 3	58 ± 1	74 ± 2	81 ± 1	88 ± 1
EPB								
	Sterilized	3.4 ± 0.5	7.7 ± 4.3	14 ± 22	49 ± 4	70 ± 1	83 ± 1	92 ± 1
	Non-sterilized	81 ± 2	87 ± 1	94 ± 1	95 ± 2	97 ± 1	98 ± 1	99 ± 1
5-TTri								
	Sterilized	15 ± 3	16 ± 2	28 ± 2	34 ± 3	48 ± 1	58 ± 3	74 ± 3
	Non-sterilized	19 ± 7	21 ± 3	32 ± 1	37 ± 6	75 ± 3	83 ± 2	87 ± 1
PMD								
	Sterilized	4.0 ± 2.6	6.5 ± 1.6	5.3 ± 2.6	7.4 ± 6.8	9.5 ± 1.0	11 ± 1	22 ± 3
	Non-sterilized	5.0 ± 2.1	9.5 ± 2.0	12 ± 5	18 ± 1	22 ± 2	27 ± 2	33 ± 7
S104								
	Sterilized	6.0 ± 1.7	11 ± 3	14 ± 3	18 ± 10	24 ± 5	33 ± 5	39 ± 7
	Non-sterilized	12 ± 8	13 ± 8	18 ± 3	27 ± 2	35 ± 12	41 ± 1	48 ± 4
TCP								
	Sterilized	11 ± 1	13 ± 2	14 ± 5	17 ± 2	28 ± 1	38 ± 2	46 ± 1
	Non-sterilized	15 ± 2	17 ± 1	21 ± 1	27 ± 7	36 ± 9	52 ± 2	78 ± 1

EOC emerging organic contaminant, *BPA* bisphenol A, *CBZ* carbamazepine, *EP* ethyl paraben, *5-TTri* 5-methyl-1*H*-benzotriazole, *PMD* primidone, *S104* Surfynol 104, *TCP* tris(2-chloroethyl) phosphate, *DEP* diethyl phthalate

degradation rates for the selected EOCs. This suggests, as previously reported, that biodegradation plays an important role in the elimination of EOCs in the terrestrial environment (Kimura et al. 2007).

For instance, the endocrine disruptor BPA exhibited a different behavior depending on the treatment. A faster dissipation rate was observed in the non-sterilized soil than in the sterilized soil (half-life values of 1.1 and >40 days, respectively). Therefore, BPA was easily biodegraded. Similar values have been obtained for agricultural soils in the literature. For example, Dodgen et al. (2014) reported BPA half-life values of 2 to 3 days in non-sterilized soils. Likewise, in their study of the adsorption and degradation of several contaminants in agricultural soils, Xu et al. (2009) reported BPA half-lives of 0.8 to 5.5 days.

In agricultural soils treated with compost, Camino-Sánchez et al. (2016) reported half-life values from 5 to 8 days. In this study, EPB exhibited low half-life values (<1 days) in non-sterilized soil. The half-life values in sterilized soil were approximately 4 days, which could indicate that other processes such as sorption and hydrolysis could be taking place, contributing to the formation of transformation products (Mitchell et al. 2014).

CBZ has been commonly reported as a highly recalcitrant contaminant and has half-life values ranging from 46 to >200 days (Kinney et al. 2006; Maeng et al. 2011; Walters et al. 2010). As seen in Fig. 1b, CBZ was highly persistent for both the sterilized and non-sterilized soils, exhibiting a degradation rate lower than 50% after 40 days. No big differences were found between the treatments, which could indicate that

Table 3 Adjusted degradation rates (k), correlation coefficients (R^2) for the three degradation kinetics, and estimated half-life values ($t_{1/2}$) for second-order kinetics in both sterilized and non-sterilized soils for all the studied EOCs

EOC	Soil	Zero order		First order		Second order		
		R^2	k (μg kg^{-1} day^{-1})	R^2	k (day^{-1})	R^2	k (μg^{-1} kg^{-1} day^{-1})	$t_{1/2}$ (day)
BPA								
	Sterilized	0.746	0.009	0.782	0.013	0.783	0.019	>40
	Non-sterilized	0.676	0.393	0.797	0.649	0.888	0.392	1.1
CBZ								
	Sterilized	0.812	0.007	0.849	0.008	0.878	0.011	>40
	Non-sterilized	0.630	0.008	0.699	0.010	0.764	0.014	>40
DEP								
	Sterilized	0.929	0.037	0.984	0.064	0.992	0.108	9.7
	Non-sterilized	0.705	0.081	0.873	0.163	0.961	0.372	3.3
EPB								
	Sterilized	0.647	0.022	0.918	0.109	0.989	0.281	3.7
	Non-sterilized	0.481	0.187	0.750	1.805	0.986	1.164	0.2
5-Ttri								
	Sterilized	0.780	0.054	0.859	0.077	0.919	0.112	10.1
	Non-sterilized	0.620	0.087	0.896	0.104	0.951	0.304	3.6
PMD								
	Sterilized	0.772	0.005	0.793	0.005	0.810	0.006	>40
	Non-sterilized	0.660	0.007	0.703	0.009	0.741	0.011	>40
S104								
	Sterilized	0.658	0.008	0.706	0.011	0.742	0.015	>40
	Non-sterilized	0.598	0.010	0.661	0.014	0.716	0.020	>40
TCP								
	Sterilized	0.757	0.010	0.830	0.014	0.902	0.020	>40
	Non-sterilized	0.720	0.025	0.820	0.037	0.883	0.057	17.7

EOC emerging organic contaminant, *BPA* bisphenol A, *CBZ* carbamazepine, *EP* ethyl paraben, *5-TTri* 5-methyl-1*H*-benzotriazole, *PMD* primidone, *S104* Surfynol 104, *TCP* tris(2-chloroethyl) phosphate, *DEP* diethyl phthalate

biodegradation does not play the most important role in CBZ degradation in soils.

Figure 1c shows that DEP had a degradation rate of more than 50% for both soil treatments and half-life values of approximately 10 days for the sterilized soil and 4 days for the non-sterilized soil. Moreover, moderate differences were observed between the soil treatments, suggesting that microorganisms contribute to the degradation of DEP.

The degradation rate for 5-TTri was more than 50% for both soil treatments (Fig. 1f). Half-life values were 10 and 3.6 days for sterilized and non-sterilized soils, respectively, and degradation was higher and faster in the non-sterilized soil than in the sterilized soil. In the literature, there are no reports on the degradation of this compound in soil. Huntscha et al. (2014) studied the biotransformation of several benzotriazoles with activated sludge and found out that the half-life value of 5-TTri was less than a day, detecting seven transformation products.

After an incubation time of 40 days, PMD exhibited a very low degradation for both soil treatments. In fact, PMD half-life values for both the non-sterilized and sterilized soil were >40 days (Fig. 1e). Nevertheless, substantial differences were not found in degradation when the soil was sterilized, suggesting that PMD biodegradation is not the most important pathway of dissipation in soil. No previous degradation experiments involving PMD in soils have been previously reported. Chen et al. (2011) studied the distribution and accumulation of organic contaminants from irrigation water in soil, detecting only 9 out of 43 contaminants in the soils.

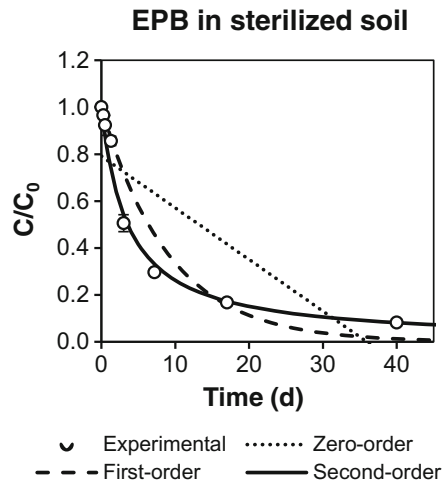

Fig. 2 Adjustment of the three different kinetics (zero-, first-, and second-order) to the experimental mean values ($N = 3$) for ethyl paraben in the sterilized soil

PMD was one of those nine contaminants, which could suggest that PMD binds strongly to soil and is not bioavailable for microorganisms.

Similar to PMD, S104 exhibited half-life values in excess of 40 days for both soil treatments (Fig. 1g). Moreover, no big differences were observed between the treatments, suggesting that S104 is not easily biodegraded.

Figure 1h shows that TCP degradation was similar for both treatments for short incubation times. However, after 20 days of incubation, TCP degradation in the non-sterilized soil increased faster than in the sterilized soil. At the end of the experiment, the degradation rates were less than 50% for the sterilized soil and less than 80% for the non-sterilized soil.

The physical-chemical properties, such as log K_{OC}, neutral log K_{OW}, solubility, and log K_{OC}, were correlated with the calculated degradation rates. However, no strong correlations were found ($R^2 < 0.2$ in all the properties; Fig. S1), which is indicative of the complexity of the contaminants' attenuation in soil.

4 Conclusions

This study showed that a sterilization treatment decreased the degradation rates for most of the selected EOCs. Therefore, biodegradation plays a significant role in the overall degradation of EOCs in soil.

In sterilized soil, after 40 days of incubation, BPA, CBZ, PMD, S104, and TCP exhibited degradation below 50%, while only DEP, EPB, and 5-TTri exhibited faster degradation. In contrast, after the same incubation time in non-sterilized soil, only three EOCs exhibited degradations below 50% (CBZ, PMD, and S104) and could thus be considered persistent contaminants in soil, while the remaining EOCs exhibited degradation rates over 70%.

Experimental degradation curves were fitted with three degradation kinetics for both the sterilized and non-sterilized soils. The second-order kinetics exhibited better correlations than the zero- and first-order kinetics. Understanding the significance of this trend requires further research.

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References

Avisar, D., Lester, Y., & Ronen, D. (2009). Sulfamethoxazole contamination of a deep phreatic aquifer. *Science of the Total Environment, 407*(14), 4278–4282.

Bell, K. Y., Wells, M. J. M., Traexler, K. A., Pellegrin, M.-L., Morse, A., & Bandy, J. (2011). Emerging Pollutants. *Water Environment Research, 83*(10), 1906–1984.

Camino-Sánchez, F. J., Zafra-Gómez, A., Dorival-García, N., Juárez-Jiménez, B., & Vílchez, J. L. (2016). Determination of selected parabens, benzophenones, triclosan and triclocarban in agricultural soils after and before treatment with compost from sewage sludge: a lixiviation study. *Talanta, 150*, 415–424.

Chen, F., Ying, G.-G., Kong, L.-X., Wang, L., Zhao, J.-L., Zhou, L.-J., et al. (2011). Distribution and accumulation of endocrine-disrupting chemicals and pharmaceuticals in wastewater irrigated soils in Hebei, China. *Environmental Pollution, 159*(6), 1490–1498.

Dodgen, L. K., Li, J., Wu, X., Lu, Z., & Gan, J. J. (2014). Transformation and removal pathways of four common PPCP/EDCs in soil. *Environmental Pollution, 193*, 29–36.

Gibson, R., Durán-Álvarez, J. C., Estrada, K. L., Chávez, A., & Jiménez Cisneros, B. (2010). Accumulation and leaching potential of some pharmaceuticals and potential endocrine disruptors in soils irrigated with wastewater in the Tula Valley, Mexico. *Chemosphere, 81*(11), 1437–1445.

Huntscha, S., Hofstetter, T. B., Schymanski, E. L., Spahr, S., & Hollender, J. (2014). Biotransformation of benzotriazoles: insights from transformation product identification and compound-specific isotope analysis. *Environmental Science & Technology, 48*(8), 4435–4443.

Kimura, K., Hara, H., & Watanabe, Y. (2007). Elimination of selected acidic pharmaceuticals from municipal wastewater

by an activated sludge system and membrane bioreactors. *Environmental Science & Technology, 41*(10), 3708–3714.

Kinney, C. A., Furlong, E. T., Werner, S. L., & Cahill, J. D. (2006). Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. *Environmental Toxicology and Chemistry, 25*(2), 317–326.

Lapworth, D. J., Baran, N., Stuart, M. E., & Ward, R. S. (2012). Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. *Environmental Pollution, 163*(0), 287–303.

Li, W. C. (2014). Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. *Environmental Pollution, 187*(0), 193–201.

Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., et al. (2014). A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the Total Environment, 473–474*, 619–641.

Maeng, S. K., Sharma, S. K., Abel, C. D. T., Magic-Knezev, A., & Amy, G. L. (2011). Role of biodegradation in the removal of pharmaceutically active compounds with different bulk organic matter characteristics through managed aquifer recharge: batch and column studies. *Water Research, 45*(16), 4722–4736.

Mitchell, S. M., Ullman, J. L., Teel, A. L., & Watts, R. J. (2014). pH and temperature effects on the hydrolysis of three β-lactam antibiotics: ampicillin, cefalotin and cefoxitin. *Science of the Total Environment, 466–467*, 547–555.

Petrie, B., Barden, R., & Kasprzyk-Hordern, B. (2015). A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. *Water Research, 72*(0), 3–27.

Schwarzenbach, R. P., Gschwend, P. M., & Imboden, D. M. (2005). Biological Transformations. In *Environmental Organic Chemistry* (pp. 687–773): John Wiley & Sons, Inc.

United Nations (2014). The United Nations world water development report 2014: water and energy. In U. N. W. W. A. Programme (Ed.). Paris: UNESCO.

Walters, E., McClellan, K., & Halden, R. U. (2010). Occurrence and loss over three years of 72 pharmaceuticals and personal care products from biosolids–soil mixtures in outdoor mesocosms. *Water Research, 44*(20), 6011–6020.

Xu, J., Wu, L., & Chang, A. C. (2009). Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. *Chemosphere, 77*(10), 1299–1305.