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# **Environmental Pollution**



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# Influence of microplastic contamination on the dissipation of endocrine disrupting chemicals in soil environment<sup> $\ddagger$ </sup>

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ARTICLEINFO	A B S T R A C T				
Keywords: Microplastics EDCs Soil dissipation Degradation kinetics First-order kinetic Biphasic kinetic.	Microplastic (MP) contamination is in the spotlight today, yet knowledge of their interaction with other organic contaminants in the soil environment is limited. Concerns extend to endocrine disrupting chemicals (EDCs), known for their potential to interfere with the hormonal systems of organisms and for their persistence and widespread presence in the environment. In this study, the most frequently occurring EDCs were monitored both in alluvial soil and in soil contaminated with different MPs commonly found in soil media, polyethylene, polyamide, and polystyrene. Bisphenol A and parabens were the most rapidly dissipating compounds, followed by triclosan and triclocarban, with the latter showing poor degradation. Per- and polyfluoroalkyl substances (PFAS) showed high persistence as concentrations remained nearly constant throughout the experiment. Although they fitted well with first-order dissipation kinetics, most showed biphasic behavior. The co-occurrence of MPs in the soil influenced the kinetic behavior in most cases although the differences were not very marked. MPs could impact sorption-desorption processes, affecting contaminant mobility and bioavailability to organisms in soil. These findings strengthen evidence for the influence of MPs on the behavior of soil contaminants such as EDCs, not only as vectors or sources of contaminants but by affecting dissipation kinetics.				

# 1. Introduction

Microplastics (MPs), plastics with particle sizes below 5 mm, have emerged as a significant global environmental concern due to their widespread presence in marine and terrestrial ecosystems, posing threats to ecosystem health (Rillig and Lehmann, 2020; Surendran et al., 2023; Vivekanand et al., 2021). MPs can act as carriers of persistent organic pollutant but also as reservoirs, leading to a dual role in environmental contamination (Arienzo et al., 2021). In terrestrial environment, soil is the major repository for MPs (Ding et al., 2021; Li et al., 2020). Multiple pathways contribute to soil contamination by MPs, including the plastic industry, the use of biosolids, wastewater irrigation, and other agricultural practices (Bläsing and Amelung, 2018; Surendran et al., 2023). Polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyamide (PA) are the most prevalent types of MPs found in soil environments (Chen et al., 2021). Once in the soil, MPs can migrate influenced by factors such as particle size and soil texture (Bläsing and Amelung, 2018), soil biota, plant root activity, and agricultural activities, among others, which highlights the complexity of interactions involved in MP pollution (Surendran et al., 2023).

MP contamination significantly impacts soil biophysics but also serves as carrier for toxic pollutants, influencing their release and accumulation in the environment. MPs alter soil properties and chemistry, affecting aggregation, water-holding capacity, microbial activity, and dissolved organic matter composition, thus impacting soil health and food production (Ding et al., 2021; Rillig and Lehmann, 2020). This disruption varies based on MP type and concentrations (Zhang et al., 2022). Moreover, MPs modify soil properties, particularly sorption capacity, influencing the mobility of organic compounds. Studies reveal that MPs can possess an adsorption capacity up to six orders of magnitude higher than other environmental matrices (Mato et al., 2001), primarily driven by hydrophobicity (Li et al., 2018; Mejías et al., 2023a, 2023b; Velzeboer et al., 2014), although water chemistry, such as like salinity, also plays a significant role (Costigan et al., 2022). Understanding these effects and interactions is crucial for effectively managing soil contamination effectively.

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The study of contaminant fate and transport in soil has gained significant attention in recent decades due to concerns about their impact on ecosystems. Among the various processes governing pollutant behavior, degradation is particularly crucial. Understanding the kinetics of degradation mechanisms in soil is essential for accurately assessing contaminant degradability. Several empirical kinetic models have been used to describe the degradation rate of contaminants in soil based on experimental data (Sarmah and Close, 2009; FOCUS, 2006). While some pollutants, such as pesticides, can be accurately described by first-order kinetics (SFO), others exhibit more complex degradation patterns influenced by factors like concentration and time, and SFO may not sufficiently represent degradation (Ma et al., 2004). When the deviation from SFO is substantial and nonlinear, with  $R^2 < 0.7$  after logarithmic transformation, various organizations and reference guidelines suggest that the model is questionable and invalid (European Commission, 2000; FOCUS, 2006). In such cases, more complex mathematical models with appropriate indices are necessary to accurately describe the persistence and dissipation kinetics of these compounds.

#### Table 1

Physical-chemical properties of target compounds.

Compound	CAS number	Molecular weight (g $mol^{-1}$ )	рК <sub>а</sub>	Log K <sub>ow</sub>	Structure
Bisphenol A (BPA)	80-05-7	228.3	10.3	3.8	носторон
Methyl paraben (MePB)	99-76-3	152.2	8.5	1.9	HO OCH3
Ethyl paraben (EtPB)	120-47-8	166.2	8.5	2.3	HO
Propyl paraben (PrPB)	94-13-3	180.2	8.5	2.9	HO
Triclosan (TCS)	3380-34-5	289.5	7.9	4.8	CI OH
Triclocarban (TCB)	101-20-2	315.6	12.7	4.3	
Perfluorooctanoic acid (PFOA)	335-67-1	414.1	2.8	6.3	FFFFFF FFFFFFFFFFFFFFFFFFFFFFFFFFFFFFF
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	500.1	<1.0	4.5	FFFFFFFFFFFFF
Perfluorobutanoic acid (PFBuA)	375-22-4	214.0	0.2–0.4	2.14	F F O F OH F F F F
Perfluoropentanoic acid (PFPeA)	2706-90-3	264.1	0.4	2.81	
Perfluorohexanoic acid (PFHxA)	307-24-4	314.1	0.42	3.48	
Perfluoroheptanoic acid (PFHpA)	375-85-9	364.1	0.47	4.15	

Azzouz et al. (2016); National Center for Biotechnology Information (2023); Mejías et al. (2023a); Regueiro et al. (2009).

Among of contaminants of significant concern are endocrine disrupting chemicals (EDCs), notable for their extensive use and occurrence in the environment. They pose a threat due to their capacity to disrupt the normal function of the hormonal systems of animals, including humans (Puri et al., 2023). EDCs represent a diverse group of contaminants commonly found in soil, including antimicrobial agents, household ingredients, personal care products, preservatives, and plastic packaging (Chen et al., 2022; Puri et al., 2023). These compounds often enter soil through wastewater influents and the application of biosolids for soil enrichment and irrigation (Popoola et al., 2023; Poustie et al., 2020). EDCs frequently coexist with MPs in soil environments. However, the influence of MPs on the degradation kinetics and dissipation behaviors of EDCs remains poorly understood. In this context, there is limited understanding of the kinetic behavior of prevalent EDCs in soil contaminated by MPs, as well as the potential influence of plastic particles on their degradation.

This study aims to investigate the kinetic properties of twelve EDCs belonging to different classes (bisphenol A (BPA), parabens, antimicrobials, and PFAS) in alluvial soil containing three representative types of MPs (PE, PS, PA). For this purpose, a series of batch experiments were conducted to assess the differences between soil amended with these MPs and soil free of MPs. The kinetics were fitted to selected models to validate the role of MPs on the dissipation of the studied pollutants, using mathematical parameters. The obtained results will contribute to a better understanding of the impacts of MPs in the soil environment.

# 2. Methods

#### 2.1. Chemicals and soil properties

The selected EDCs compounds were BPA, methyl paraben (MePB), ethyl paraben (EtPB), propyl paraben (PrPB), triclosan (TCS), triclocarban (TCB), perfluorooctanesulfonic acid (PFOS); perfluorooctanoic acid (PFOA), perfluorobutanoic acid (PFBuA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid (PFHpA). Table 1 lists the compound names, CAS number, main physicochemical properties, and their chemical structure.

Studied agricultural soil was collected from a non-contaminated and controlled experimental area sited in Seville (SW Spain). It was an alluvial soil type widely extended in the plain of the main rivers from Europe. Ten kilograms of the soil was collected from the surface layer (0–20 cm), homogenized, sieved (particle size <2 mm) and stored in glass bottles at -18 °C until the batch experiments.

The soil features were assessed through the determination of the texture, pH, electrical conductivity (EC), organic matter content (OM), cationic exchange capacity (CEC), and exchangeable cations content ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$ ). Moreover, the soil was analyzed to ensure the absence of target compounds. Soil characteristics and more details about the applied analytical methods can be found in Supplementary Material.

#### 2.2. Batch experiments

Batch experiments were carried out according to OECD guideline 307 (OECD, 2002). All experiments were done by quintuplicate using soil spiked with target compounds setting the same concentration for each studied compound (in the range  $0.5-6 \ \mu g \ g^{-1}$ ) and under climatic conditions controlled by a climatic chamber. The reactors containing 250 g of spiked soil were fixed as follow: five using soil non-contaminated with MPs, the others 15 reactors were contaminated with 2.5 g of PA (50  $\mu$ m), PE (300  $\mu$ m), and PS (900  $\mu$ m) equivalent to 1% w/w. The soils were spiked with target compounds using an aqueous solution containing the minimum volume of methanol possible to prevent any influence on soil microbial activity. Therefore, aliquots of 25 mL of a working solution containing the studied compounds were mixed with 2.5 g of microplastic in glass bottles. The mixture was mechanically

shacked at 350 rpm using a multistirrer magnetic device (Selecta, Multimatic 9N, Spain) for 24h. Then, the mixtures were added to portions of 250 g of the soil in reactors and 25 mL of deionized water was added to obtain a final soil humidity of 20 %.

For each microplastic type, batch experiments were carried out by quintuplicate and analyzed by duplicate. Two reactors were fixed with non-spiked soil. Moreover, blank reactors were fixed with soil spiked with target compounds without microplastic (by quintuplicate). Soil non-contaminated with MPs was treated the same but without the addition of MPs.

Experiments were carried out under aerobic conditions in a climate chamber (Selecta, Barcelona, Spain) with 33% of relative humidity, 20% of soil humidity and irradiation levels of 1091 W m<sup>-2</sup>. These conditions were selected according to the typical Mediterranean climate. Soil humidity was checked by gravimetry and corrected by the addition of distilled water.

One hundred and twenty-three samples (2.0 g) were collected from each reactor as follows: five weekly samples were collected during first 25 days; three weekly samples from days 26–39, two weekly sample from days 40–67; one sample at the following 28 days (from days 68–96) and one sample every two weeks from days 97–123. Samples were freeze-dried in a cryodos-50 (Telstar, Terrasa, Spain) lyophilizer, sieved (particle size <2 mm) and stored at -18 °C until analysis.

# 2.3. Soil treatment and LC-MS/MS analysis

The method was based on ultrasonic-assisted extraction, clean-up by dispersive solid-phase extraction, and determination by liquidchromatography-tandem mass spectrometry as it was described by Abril et al. (2018). One gram of lyophilized samples was extracted using two 3 mL portions of MeOH:HAc (95:5, v/v) by sonication. Then, the combined extracts were subjected to a clean-up based on dispersive solid-phase extraction using 800 mg of C18 as clean-up sorbent. The organic phase was separated by centrifugation and evaporated to dryness using a gentle nitrogen stream. The dried extract was reconstituted in 250  $\mu$ L of MeOH:water solution (1:1, v/v), filtered, and 10  $\mu$ L injected in the LC-MS/MS system.

The analysis was carried out by liquid-chromatography tandem mass spectrometry in a 1200 Series liquid chromatograph (Agilent, Santa Clara, USA) coupled to a 6410-triple quadrupole (QqQ) mass spectrometer (MS) equipped with an electrospray ionization source that was used for chromatographic determination. More details about the analytical method can be found in Supplementary Material.

#### 2.4. Method performance and quality control

Applied analytical method was validated by the determination of matrix effect, linearity, method detection limit (MDL), method quantification limit (MQL), precision, and accuracy. Full detail about the validation of the method is described by Abril et al. (2018). A brief description can be read in Supplementary Material. The analysis was carried out using matrix-matched calibration curves. The calibration curves were constructed using at least seven calibration standards prepared by triplicate using blank soil in the range from 0.01 to 500  $\mu$ g kg<sup>-1</sup> d.m. Recoveries of target compounds were from 74 to 111 %, accuracy was 87–100 % and limit of detection and quantification were lower than 0.75 and 2.51 ng g<sup>-1</sup> for all compounds, except BPA (3.82 and 12.7 ng g<sup>-1</sup>, respectively).

For each batch of samples, matrix-matched calibration standards, spiked quality control samples and procedural blanks were measured together with the samples collected from the reactors. The recoveries of target compounds were determined and compared with those obtained during the validation of the method. Moreover, the lack of analytes in blank reactors and on the procedural blanks was verified. The concentrations of all studied compounds were below the limits of detection in both blank reactors and in the procedural blanks.

# 2.5. Dissipation kinetic models

The study of the dissipation kinetics of the target EDCs in the different conditions (soil, soil + PE, soil + PA, and soil + PS) was performed following the FOCUS guideline (FOCUS, 2006) and published research for environmental pollutants (Santos et al., 2023; Sarmah and Close, 2009; Srinivasan et al., 2014). The measured data sets of each of the investigated compounds were fitted to five models: a single first-order (SFO); three biphasic kinetic models, the bi-exponential model (BEM), the first-order double-exponential decay model (FODED), and the first-order two-compartment model (FOTC); and a model describing a lagged dissipation pattern, the logistic model (LM). These models were chosen for their simplicity and with the aim of covering the three possible scenarios, especially suitable for highly persistent compounds. The models were compared in terms of their representation, the statistical parameters, and the calculation of the estimated DT<sub>50</sub> and DT<sub>90</sub> times, which represent the dissipation of the 50% and 90% of the initial concentrations, respectively.

#### 2.5.1. Single first-order kinetic model (SFO)

This is the simplest kinetic model and is expressed by an equation with only two parameters. An exponential decay model assumes that the number of contaminant molecules in the soil is small relative to the number of active sites in the soil. Consequently, the ratio decreases proportionally to the remaining concentration of the compound. The time required to reduce the concentration by a given % is constant throughout the experiment and independent of the initial concentration of the contaminant. The exponential equation for this model is (1):

$$C = C_0 e^{-k_1 t} \tag{1}$$

where C is the concentration ( $\mu g kg^{-1}$ ) at time t (day) after application, C<sub>0</sub> is the initial concentration ( $\mu g kg^{-1}$ ), and k<sub>1</sub> is the first-order rate constant (day<sup>-1</sup>).

#### 2.5.2. Bi-exponential model (BEM)

According to this model, degradation occurs in two compartments (Srinivasan et al., 2014). In the first compartment, a rapid degradation takes place. This compartment corresponds to the soil-water phase, where contaminants are accessible to microorganisms. A slow degradation is expected in the second compartment. This compartment represents a phase where contaminants are adsorbed on soil particles, and dissipation is governed by the slow desorption-diffusion mechanism.

In this model, the dissipation rate it is defined by the sum of first and second order differential equation (2):

$$\frac{dC}{dt} = -\left(k_1C + k_2C^2\right) \tag{2}$$

The integrated equation results in:

$$e^{-k_1 t} = \frac{C(k_1 + k_2 C_0)}{C_0(k_1 + k_2 C)}$$
(3)

The rearrangement this yields the following equation:

$$C = \frac{K_1 C_0}{(K_1 + K_2 C_0)e^{k_1 t} - k_2 C_0}$$
(4)

where C is the concentration ( $\mu g kg^{-1}$ ) at time t (day), C<sub>0</sub> is the initial concentration ( $\mu g kg^{-1}$ ), k<sub>1</sub> is the first order rate constant (day<sup>-1</sup>), and k<sub>2</sub> is the second order rate constant (kg  $\mu g^{-1} day^{-1}$ ). The equation simplifies to a single first-order equation when k<sub>2</sub> = 0. It is important to emphasize that although the equation is referred to as a biexponential, its integrated expression is not the sum of two exponential terms.

#### 2.5.3. First-order double-exponential decay model (FODED)

Similar to the BEM model, this model assumes that contaminant concentrations are distributed between two compartments: a phase in which the compounds are dissolved (solution phase) and a phase in which they are adsorbed onto soil particles (sorbed phase). However, the FODED model involves first-order kinetics for both processes.

The equation can be written as (5):

$$C = C_{Sol}e^{-k_1t} + C_{Sorb}e^{-k_2t}$$
(5)

where  $C_{Sol}$  is the concentration of the compound initially distributed in the solution phase;  $C_{Sorb}$  is the concentration of the compound adsorbed on soil particles;  $k_1$  (day<sup>-1</sup>) and  $k_2$  (day<sup>-1</sup>) are the dissipation rate constants for each compartment, and t is time (day).

Typically,  $k_1$  is higher than  $k_2$ , which indicates that the degradation of the contaminants in the solution compartment is faster than the degradation of those adsorbed on the soil. Furthermore, if  $k_1$  is equal to  $k_2$ , or if one of the concentrations (C<sub>Sol</sub> or C<sub>Sorb</sub>) is zero, the model undergoes a mathematical transformation to the SFO model (Santos et al., 2023).

# 2.5.4. First-order two-compartment model (FOTC)

Hill and Schaalje (1985) originally proposed this model to elucidate the processes of both slow and rapid dissipation of pesticides. Describes degradation in complex systems such as the soil environment. Like FODED, dissipation occurs in two compartments. In the first compartment, degradation is rapid and driven by physical, chemical, and other processes; while in the second compartment, degradation is slow and driven primarily by microbial, chemical, or enzymatic processes. However, the FOTC model incorporates a transfer rate component between the two compartments, a feature that is not accounted for in the other two-phase models mentioned above (Briones and Sarmah, 2019).

The equations are expressed as:

$$\frac{dC_1}{dt} = -(k_1 + k_r)C_1 \tag{6}$$

$$\frac{dC_2}{dt} = k_r C_1 - k_2 C_2 \tag{7}$$

where  $C_1$  is the concentration in the first compartment;  $C_2$  is the concentration in the second compartment;  $k_r$  (day<sup>-1</sup>) is the transfer rate constant of the compound between the two compartments;  $k_1$  (day<sup>-1</sup>) and  $k_2$  (day<sup>-1</sup>) are the rate constants for the fast and slow degradation compartments, respectively; and t is the time (day). Since degradation in the first compartment is faster than in the second one,  $k_1$  must be greater than  $k_2$ . Normally,  $K_r$  is greater than 0. The total concentration in the soil at a given time is the sum of  $C_1$  and  $C_2$  (Sarmah and Close, 2009).

The integration of the two differential equations results in:

$$C = C_0 e^{-(k_1 + k_r)t} + C_0 \frac{k_r}{k_1 + k_r - k_2} \left( e^{-k_2 t} - e^{-(k_1 + k_r)t} \right)$$
(8)

## 2.5.5. Logistic model (LM)

The logistic model (LM) assumes that concentrations may be constant for a period of time, and after sludge or compost application, the degradation rate constant increases up to a maximum value. This could be related to the increase in degradation activity of the microorganisms. The initial phase is known as the lag-phase (FOCUS, 2006).

The equation is the following:

$$C = C_0 \left( \frac{a_{max}}{(a_{max} - a_0 + a_0 e^{rt})} \right)^{\frac{a_{max}}{r}}$$
(9)

where C is the concentration at time t (day),  $C_0$  is the initial concentration (t = 0),  $a_0$  is the kinetic constant at the beginning of the batch experiment,  $a_{max}$  is the maximum value of the kinetic constant, r is the microbial growth rate, and t is time (day). For this model, when the maximum degradation rate is reached, the kinetics becomes first order, i.e., when  $a_0 = a_{max}$ . The higher the values of r or  $a_0$ , the shorter the lagphase of the compound.

# 2.6. Fitting of data to models and calculating endpoints

Fitting of the experimental data of the concentrations measured throughout the experiment was performed first visually, and then using the Solver add-in of the Microsoft Excel software.

The visual fit was evaluated according to the recommendations of the FOCUS guide for each model. For this purpose, the averages of the experimental concentrations were plotted as a function of time, and as a function of the concentrations obtained in the models. Goodness of fit was assessed by the coefficient of determination ( $R^2$ ) and the slope of this second plot, which should ideally be 1.

The most accurate fit was performed using the Solver program, which provides the best fit of the parameters by minimizing the sum of squares of the residuals (SSR) (the mean of the squared error) between the measured and model values.

The optimized parameters for each model were as follows:  $C_0$  and  $k_1$  in the SFO;  $C_0$ ,  $k_1$  and  $k_2$  in the BEM;  $k_1$ ,  $k_2$ ,  $C_{Sorb}$ , and  $C_{Sol}$  in the FODED,  $C_0$ ,  $k_1$ ,  $k_2$ , and  $k_r$  in the FOTC, and  $C_0$ ,  $a_{max}$ ,  $a_0$  and r in the LM.

Once the modeling was fitted, the of 50% (DT50) and 90% (DT90) dissipation times were estimated for each EDC in each of the batch experiment conditions. In the case of SFO, the times were calculated by using the following equations (Kodešová et al., 2016; Sarmah and Close, 2009):

$$DT50 = \frac{\ln 2}{k_1}$$
$$DT90 = \frac{\ln 10}{k_1}$$

For the other the models, since there is no formula to estimate these times, the values were calculated using an interactive Excel procedure, the Goal Seek function, which searches for the value (that an input must have) to achieve the desired output. The optimized parameters for each individual model described above ( $C_0$ ,  $K_r$ ,  $a_{max}$ , etc.) were utilized in this function to calculate and estimate the DT50/DT90 values for all compounds withing the respective model.

#### 3. Results and discussion

#### 3.1. Degradation of EDCs in soil

The batch experiments were conducted on alluvial soil, which was previously spiked with the compounds of interest. The non-spiked and MP-free soil blanks were simultaneously analyzed and processed in the same manner as the rest of the reactors in the climate chamber. TCS and TCB were quantified in non-spiked soil blanks at mean concentrations of 67.5  $\mu$ g kg<sup>-1</sup> and 23.9  $\mu$ g kg<sup>-1</sup>, respectively; PFAS were present but below the MQL in all cases; parabens and BPA were not detected.

These concentrations were compared with those previously reported in the literature. The amount of TCS was higher than that quantified in soils from agricultural areas in Michigan (0.55–3.5  $\mu g \; kg^{-1})$  (Olaniyan et al., 2016) and agricultural areas where biosolids were added in Kuna, Idaho  $(2.7-4.4 \,\mu g \, kg^{-1})$  (Sherburne et al., 2016), but significantly lower than other soils amended with digested or composted sludge  $(833-14000 \ \mu g \ kg^{-1})$  (Mejías et al., 2021); however, levels were comparable in some cases lower than those found in agricultural soil samples collected from India (MLQ – 921.6  $\mu$ g kg<sup>-1</sup>) (Saha et al., 2022). The concentrations of TCB were similar to those documented in agricultural soils by Sherburne et al. (2016), ranging from 14.8 to 27.3  $\mu$ g kg<sup>-1</sup>. Notably, the concentrations of TCB in this study were considerably lower than those of TCS, which is consistent with the results reported by Saha et al. (2022). For the remaining EDCs, only PFAS were detected. PFAS concentrations in soil are typically lower compared to antimicrobials based on previous research. For example, Wellmitz et al. (2023) analyzed a total of 11 soils belonging to different German ecosystems for 24 PFASs; some soils were free of PFAS and others showed **SPFAS** 

concentrations ranging from 0.31 to 19.7  $\mu g~kg^{-1}$ , levels that hardly changed in two decades. Differences between the concentration levels of EDCs in the studied alluvial soil and similar studies may result from differences in the pathways of entry into the terrestrial environment, the wastewater treatment methods, and the prevailing environmental conditions.

The concentrations found were not significant for the study, considering the high concentrations at which the soil was initially enriched for the batch experiments. The concentrations of each compound studied were measured for a total of 123 days. The degradation behavior differed depending on the compound studied. BPA and parabens displayed a significant decrease in their concentrations after 120 days, TCS showed a slower degradation maintaining 30–50% of the initial concentrations while TCB and perfluorinated compounds hardly were hardly degraded showing similar or slightly lower concentrations at the end of the experiments. The kinetic models described in section 2.5 were applied to their degradation. Tables S4–S7 present all the kinetic parameters optimized for each EDC in each experimental condition for each of the kinetic models.

# 3.2. Dissipation of BPA

The average initial concentration of BPA in the spiked soil samples ranged from 84.2  $\mu$ g kg<sup>-1</sup> to 382.7  $\mu$ g kg<sup>-1</sup>. The concentrations measured for BPA during the batch experiments are shown in Fig. 1.

As for the dissipation kinetics, the LM model was transformed into a SFO model, in soil without and with MPs, considering the optimized parameters ( $a_{max} = a_0$ ). On the other hand, the FODED and FOTC models showed biphasic kinetics in all cases taking place in two compartments: a rapid degradation in the first one at the beginning (in the solution phase or deposited compartment) followed by a slow degradation (in the sorbed phase or retained compartment). This is because these models have accounted for the concentration on the first day. Therefore, according to these models, the initial concentrations were much higher compared to SFO (e.g., 12501 µg kg<sup>-1</sup> vs 54 µg kg<sup>-1</sup> in MP-free soil). However, this was not the case for the BEM model, which expects rapid degradation to occur between the soil-water phase, where microorganisms have easy access; only in the soil with PE was the kinetic behavior biphasic, where  $k_1 > k_2$ .

The fit of the experimental data to the kinetic models, was evaluated by the calculated coefficients of determination and the slopes obtained, which estimate how well the experimental concentrations fit the concentrations calculated by the models. Good fits were obtained with all models. The fit to SFO kinetics yielded coefficients of determination ranging from 0.630 to 0.868 and the fit to FODED and FOTC ranging from 0.872 to 0.981, which would indicate that BPA may follow a biphasic kinetics with two compartments.

For the endpoints, the  $DT_{50}$  was 14.5 days and the  $DT_{90}$  was 48.3 days using the SFO model, in agreement with similar kinetic studies. Wang et al. (2023) obtained a  $DT_{50}$  of 14.8 days for BPA degradation in flooded soil when fitting the data to SFO. Nevertheless, this time was reduced to 4.9 days when rice plants were grown, which provided a more favorable environment for the degradation of the compound. Hence, it is important to note that the degradation of BPA can be strongly influenced by the presence of oxygen, microbial activity and other factors, and that values may vary under different conditions (Wang et al., 2023). On the other hand, very short times were obtained when fitting to compartmental kinetic models ( $DT_{50}$  of 0.13 days and  $DT_{90}$  of 0.44 days), due to the rapid initial degradation.

While the soil contaminated with MPs does not appear to significantly impact the kinetic behavior of BPA degradation (they fit the same models well), there are potential influences that warrant consideration. Notably, the endpoint values derived for soil containing PA following the SFO were 22.8 days and 75.8 days for  $DT_{50}$  and  $DT_{90}$ , respectively. These values were higher than those observed in soil without MPs and with PE and PS, suggesting a potential slowdown in degradation. This



Fig. 1. Mean contents of BPA as a function of time during the batch experiment in alluvial soil with fit for kinetic models: without MPs (BS), containing polyethylene (PE), polyamide (PA), and polystyrene (PS). BEM: bi-exponential model; FODED: first-order double-exponential decay; FOTC: first-order two-compartment; LM: logistic model; SFO: single first-order.

observation is further supported by the comparison average concentrations of BPA in the soil with PA (Fig. 1), revealing higher concentrations in the latter days of the experiment compared to the other conditions, which supports these results. amended soil, which could be enhanced by the presence of MP. Tang et al. (2023) explored the sorption-desorption behavior of BPA on various materials, including PA and soil. They observed significantly higher BPA retention in soil with PA compared to soil alone (2-3-fold), possibly due to differences in physicochemical properties and

This observation may be a result of increased BPA retention in PA-



Fig. 2. Mean contents of parabens as a function of time during the batch experiment in alluvial soil with fit for kinetic models: without MPs (BS), containing polyethylene (PE), polyamide (PA), and polystyrene (PS). BEM: bi-exponential model; FODED: first-order double-exponential decay; FOTC: first-order two-compartment; LM: logistic model; SFO: single first-order.

interaction mechanisms. BPA sorption in soil is mainly hydrophobic, with limited hydrogen bonding involving organic matter, whereas in PA hydrogen bonding plays a more relevant role, resulting in stronger interactions (Tang et al., 2023). Consequently, BPA desorption from soil is higher than from PA due to the strong BPA-PA interactions, reducing its availability in the liquid phase. These findings align with the FODED model, suggesting rapid degradation kinetics of BPA in the liquid phase and slower degradation in the retained phase. Notably, the estimated retained concentration (C<sub>Sorb</sub>) is 184  $\mu$ g g<sup>-1</sup> in soil with PA, as opposed to 37.7  $\mu$ g g<sup>-1</sup> in soil alone (Table S5).

# 3.3. Dissipation of parabens

The average initial concentrations in the batch experiments were between 20.7 and 55.3  $\mu$ g kg<sup>-1</sup> for MePB, between 41.1 and 84.5  $\mu$ g kg<sup>-1</sup> for EtPB, and between 4.9 and 13.6  $\mu$ g kg<sup>-1</sup> for PrPB. The measured concentrations for the parabens over the 120 days are presented in Fig. 2.

These average concentrations measured for the parabens were considerably low considering the amounts added at the beginning of the experiment. The low values could be due to a rapid degradation of the compounds, and especially of PrPb, only a few hours after the spiking process, as also described in similar studies (Malvar et al., 2021; Wu et al., 2017).

Considering the dissipation kinetics of these compounds in soil (free of MPs), a similar behavior was observed among them, which is consistent with the SFO kinetics (Fig. 2). Due to the rapid degradation during the first hours, the plotted data would show the bottom plot of a first-order kinetics. Those with  $R^2 > 0.7$  for MePB and PrPB show a good fit, but not for PrPB that despite the visual fit, the low concentration values would prevent its correct fit to the model.

On the other hand, a similar fit was also obtained for the applied twophase models (FODED and FOTC kinetics). The good fit for these models could be due to the initial rapid degradation that occurs after a few hours of adding these compounds to the soil, followed by a slower degradation according to the optimized parameters ( $k_1 > k_2$  in the FODED and FOTC models in all cases).

A trend in the dissipation of parabens correlated with their alkyl chain length is also observed. A lower degradation is observed when considering the SFO model as the number of C in the chain increases (kinetic constants of MePB > EtPB > PrPB); this is also reflected in the endpoints, obtaining DT<sub>50</sub> values of 17.5 days, 31.8 days, and 69.9 days, and DT<sub>90</sub> values of 58 days, 106 days, and 230 days for MePB, EtPB, and PrPB, respectively. This trend does not appear to be followed according to the optimized parameters for the two-phase models, probably due to the rapid degradation occurring in the first stage, which is drastically higher for PrPB compared to the other two parabens. This results in results in DT<sub>50</sub> < 1 day for all parabens. However, the trend seems to be fulfilled in the slow degradation stage, with DT<sub>90</sub> values of 22–24 days, 60–66 days, and 156–158 days being obtained for MePB, EtPb, and PrPB, respectively.

As for the LM model it transformed to SFO in the case of MePB ( $a_{max} = a_0$ ), showed a strong lag-phase in dissipation (until day 60) in the case of EtPB and showed a slight lag phase in the case of PrPB, although the fit in the latter two cases (visual and statistical) was not good ( $R^2 < 0.6$  and slopes <0.62). Similarly, the endpoints were like those obtained with SFO, with  $DT_{50}$  of 17.5 days for MePB, 65.7 days for EtPB and 77.6 days for PrPB.

Regarding the influence of the presence of MPs, it was observed that MePB dissipation kinetics is faster in soil with MPs, especially with PE and PS. The SFO kinetics in blank soil was 0.04 vs. 0.154 and 0.285 in soil amended with PE and PS, respectively. Soil behavior with PA is similar to that of MP-free soil. A better fit is observed with biphasic models: very fast degradation at the beginning followed by slower degradation. This is more pronounced than in soil free of MP-free soil, especially in soil amended with PE and PS ( $R^2 > 0.9$ ). The fit is lower in

PS probably because of the higher dissipation of the data. In general, a higher dissipation is observed in soil amended with MPs, giving shorter  $DT_{90}$  values in the SFO and biphasic models.

As for EtPB, the dissipation kinetic is slightly faster (higher  $k_1$ ), except in soil with PS which is similar to the blank soil. A clearly better fit is shown with two-phase models ( $R^2 > 0.94$ ) in FODED and FOTC. The endpoints are considerably lower in soil with MPs in all models, although in the case of PS they are like those of the blank.

In the case of PrPB, dissipation occurs at a slower rate. Only the soil with PA shows a higher kinetic constant. Soils amended with PE and PA demonstrate a more robust biphasic fit, while soil with PS exhibits significant data dispersion. The fit is similar for SFO and biphasic models.

The LM model becomes SFO with MPs, except for PS, which changes but may be due to data dispersion.

In general, the data from PBs show faster degradation kinetics in soils containing MPs, with shorter endpoints with respect to soil without MPs. The kinetics fit well with the SFO model, but better with the biphasic models ( $R^2 > 0.9$ ). PrPB shows slower kinetics, compared to MePB and EtPB. As in the blank soil, degradation is slower with increasing alkyl chain length. The LM model becomes SFO with MPs, except for PS which differs but may be due to data dispersion. The hydrophobicity of the organic compound mainly determines its adsorption potential on MPs. The adsorption is therefore related to the log K<sub>ow</sub>. Velzeboer et al. (2014) found that the adsorption of 17 polychlorinated biphenyls on MPs is linear as a function of the hydrophobicity of the compound; similarly, Li et al. (2018) reached the same conclusion for 5 antibiotics, and Mejías et al. (2023a, 2023b) for 6 perfluoroalkyl substances and 4 parabens, in agreement with this study.

#### 3.4. Dissipation of triclosan and triclocarban

Average concentrations at the beginning of the batch experiments ranged from 4033 to 4651  $\mu$ g kg<sup>-1</sup> for TCS and from 1012 to 1289  $\mu$ g kg<sup>-1</sup> for TCC. TCS concentrations in the MP-free soil were reduced by 50% from the initial values at the end of the experiments, whereas TCB concentrations remained almost invariant during the assay. Fig. 3 shows the kinetic of dissipation of these two biocides.

As for the dissipation kinetics of TCS, all models were transformed into a SFO according to the optimized parameters (low  $k_2$  in BEM model, low  $k_2$  in FODED,  $k_1 = k_2$  in FOTC), except the LM model. In this model, the low value of r (related to the growth of microorganisms) and the low  $a_0$  obtained indicate a certain lag phase. The fitting of the experimental data to the examined models did not show significant differences between them. On the other hand, TCB was persistent with no apparent degradation at the end of the experiment. As for the endpoints, the estimated half-life  $DT_{50}$  for TCS was between 106 and 159 days, in contrast to TCB, whose values ranged from 176 days to more than 1000 days. It was reported that the half-life of the TCB in the soil exceeded 165 days which is in line with our results. In a similar study, Cheng et al. (2022) reported less than 20% TCB degradation in soil after 90 days of the experiment. This differs from our results on blank soil which could be due to the greater variability of the data in this particular case.

In this sense, it is worth noting that the persistence of these chemicals may be underrepresented. Residues that persist naturally in the soil and are sorbed to the organic fraction are likely to be less bioavailable compared to freshly added compounds. However, the endpoints determined in the present study are align with findings reported in previous studies (Al-Rajab et al., 2015).

The dissipation of TCS and TCB has been more extensively investigated compared to other selected organic compounds in this study. The observed dissipation pattern, where TCS exhibit more noticeable degradation compared to the nearly negligible dissipation of TCB, suggests a potential influence of microorganism mediated degradation, a process that is significantly delayed. Al-Rajab et al. (2015) concluded that TCS might be more susceptible to biodegradation by microorganisms, with soil contact identified as a key factor influencing the



Fig. 3. Mean contents of TCS and TCB as a function of time during the batch experiment in alluvial soil with fit for kinetic models: without MPs (BS), containing polyethylene (PE), polyamide (PA), and polystyrene (PS). BEM: bi-exponential model; FODED: first-order double-exponential decay; FOTC: first-order two-compartment; LM: logistic model; SFO: single first-order.

dissipation kinetics. Conversely, TCB was inherently more recalcitrant to degradation and was less influenced by soil contact. This difference in degradation susceptibility may explain the observed higher persistence of TCB in the soil.

The addition of MPs into the soil has been demonstrated to exert an influence on the dissipation kinetics of these compounds. For example, in soils contaminated with PE and PS, the reduction of TCS concentrations was 20% higher with respect to soils without MPs. In contrast to the soil with PA, TCS showed a similar behavior to the blank soil. A similar behavior was observed with TCB which was reduced by about 40% at the end of the experiment in the soil contaminated with MPs, in contrast to the soil without MPs, where the concentration hardly varied. Again, it is worth mentioning that in this study the persistence of TBC in blank soil was greater than expected.

Regarding the fit of the experimental data, the two-phase compartmental models showed an improved fit in these two soils. On the other hand, in the soil with PA all models were transformed to SFO. The fastest dissipation was shown by the soil with PE, with a  $k_1$  of 0.49 in the SFO model. These possible differences in dissipation resulted in reduced halflives in the soil with PE and PS, especially in the former whose  $DT_{50}$  ranged between 13 and 18 days. In the case of TCB the kinetic behavior does not seem to be affected by the presence of MPs; only the  $DT_{50}$  of the FODED and FOTC models were significantly reduced in the soil with PS, but this could be due to the dispersion of the data at the beginning of the experiment. Chen et al. (2021) found that TCS has a greater adsorption preference to MPs than to soil, with a greater preference to PE. These differences in adsorption-desorption behavior between MPs and soil could explain the slight change in TCS in soil with MPs input.

# 3.5. Dissipation of perfluoroalkyl compounds

The measured average concentrations of PFAS were in the range of 1480  $\mu$ g kg<sup>-1</sup> and 7700  $\mu$ g kg<sup>-1</sup> at the beginning of the batch experiments. In general, PFAS were found to be highly persistent as the

concentrations hardly varied over time. The dissipation kinetics of PFOS and PFOA are shown as representative compounds of the group, as they are the most widely used and most prevalent in the environment (Fig. 4). PFBuA, PFPeA, PFHxA, PFHpA showed the same kinetic behavior (data not shown); the concentrations of the latter are included in the Supplementary Material (Figs. S1–S4). Concentrations in the second half of the experiment remained invariant.

A good fit to the models was not observed due to the high stability of these compounds. The data resulted in endpoints exceeding 1000 days in virtually all cases (except for the soil with PE). Sun et al. (2024) investigated the adsorption of PFASs on PA, on soil with PA, and on soil. The authors found that the addition of PA to soil (even as low as 1%) significantly increased PFAS adsorption. Despite the evidence for the influence of MPs on the adsorption-desorption of these substances in soil, the data from this study may indicate that MPs would have a little impact on their dissipation kinetics. Only the addition of PE increased  $k_1$ , which would indicate that it could favor degradation. The half-lives

were reduced accordingly (<1000 days), but more research is needed in this direction.

# 4. Conclusions

In conclusion, this study provides insights on the dissipation kinetics of commonly encountered EDCs in the presence of prevalent MPs in alluvial soil. The batch experiments performed for more than one hundred days under Mediterranean climate conditions with the subsequent application of kinetic models allowed for a detail assessment of the impact of MPs on the dissipation behavior of the target analytes.

The initially EDCs concentrations found in non-spiked soil were consistent with the documented levels from previous studies and variations in soil adsorption where observed, as different concentrations were quantified on the first day of the experiment. BPA and parabens exhibited rapid degradation, with BPA following a two-phase model featuring two compartments. Parabens demonstrated swift degradation,



Fig. 4. Mean contents of PFOS and PFOA as a function of time during the batch experiment in alluvial soil with fit for kinetic models: without MPs (BS), containing polyethylene (PE), polyamide (PA), and polystyrene (PS). BEM: bi-exponential model; FODED: first-order double-exponential decay; FOTC: first-order two-compartment; LM: logistic model; SFO: single first-order.

showing SFO, FODED, or FOTC kinetics, and a correlation between dissipation rate and alkyl chain length was observed, potentially linked to increased adsorption capacity at higher log  $K_{ow}$  values. TCS experienced a 50% reduction, and TCB concentrations remained relatively stable in soil, although a more significant reduction was noted in the presence of MPs. Conversely, PFAS exhibited high persistence with minimal change in concentrations. The variations in soil adsorption coupled with distinct degradation patterns among the investigated EDCs underscore the complexity of the interactions within this environmental system.

Our investigation identified differences between blank soil and soil containing MPs, suggesting a potential influence of MPs on the degradation dynamics of these contaminants in the soil environment. The addition of PA increased the endpoints of BPA, potentially indicating enhanced retention in soil due to stronger interactions between BPA and the MP particles. Paraben dissipation was notably higher in soil contaminated with MPs, particularly for shorter chain parabens, resulting in shorter endpoints compared to soil without MPs. The presence of MPs was also associated with increased dissipation of TCS and TCB, with a more pronounced effect on the former biocide. Lastly, little influence of MPs was observed in the dissipation of PFAS. However, further studies are essential to understand the complex interactions and the presumed impact on the adsorption capacity in soil.

Our finding suggest that the presence of MPs induce disparities in the adsorption capacity between regular soil and soil contaminated with MPs. The potential heightened affinity of contaminants for adsorption onto MPs may lead to increased accumulation in MP-contaminated soils, elevating the risk of mobility and subsequent bioavailability to soil organisms. Moreover, factors such as soil conditions and properties, organic matter content, physicochemical properties of the contaminants, and the distinctive characteristics of each type of MP may contribute to the degradation process. These variables add complexity, rendering the field challenged and convoluted for research.

The implications of this research extend beyond the study of individual organic contaminants, highlighting the necessity of consider the co-occurring pollutants with MPs in soil environments. Nonetheless, further studies are required, especially to better elucidate the interaction mechanisms among the investigated MPs, contaminants, and soil. This research provides valuable insights into the influence of MPs on the degradation of the most prevalent EDCs in the environment. The findings not only advance our understanding of environmental processes but also underscore the need for sustainable practices and for informing strategies related to soil management and pollutant remediation.

# CRediT authorship contribution statement

Laura Martín-Pozo: Writing – original draft, Resources, Investigation, Formal analysis. Carmen Mejías: Investigation, Formal analysis. Juan Luis Santos: Writing – original draft, Methodology, Conceptualization. Julia Martín: Writing – review & editing, Methodology, Conceptualization. Irene Aparicio: Writing – review & editing, Validation, Supervision. Esteban Alonso: Project administration, Funding acquisition.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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#### Appendix B. Supplementary data

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