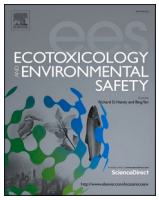
Ecotoxicology and Environmental Safety 302 (2025) 118640

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Thermodynamic modelling of pharmaceutical sorption in soil systems: A comparative study of batch and fixed-bed approaches

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ARTICLE INFO

Keywords:
Retention of soil
Transport dynamics
Temperature-dependent sorption
Fixed-bed simulation

ABSTRACT

In agricultural areas, daily and seasonal temperature fluctuations can swiftly alter the mobility of pharmaceuticals in the topsoils. Therefore, developing a method that can accurately estimate the fate and transport of terrestrial contaminants like organic micropollutants is crucial. Fixed-bed systems provide a non-traditional understanding of thermodynamic calculations and better reflect the natural conditions of the soil environment than the batch method hitherto used. To demonstrate this, the sorption behaviour of three pharmaceuticals was investigated in fixed-bed and batch experiments at five pre-measured topsoil temperatures and analysed chemometrically. The fixed-bed method accurately predicts the directly relevant chemical behaviour of pharmaceuticals in the cultivated soil layer, outperforming batch methods in correlating sorption and thermodynamics data. Opposite trends were found between the standard Gibbs' free energy (ΔG^0), and maximum saturated amount, and this ΔG^0 and total desorption in the fixed-bed experiment, while with batch, no significant relationship appeared. Thermodynamic results in the fixed-bed simulation indicate that 17α-ethynylestradiol and lidocaine-hydrochloride have negative entropy values owing to their physicochemical properties and competitive relationship, indicating a more specific surface reaction than diclofenac-sodium. The physical nature of sorption was observed in all cases, resulting in rapid and reversible adsorption processes. The application of fixed-bed systems instead of batch experiments provides new insights into soil-pharmaceutical interactions, demonstrating that fixed-bed systems more accurately model sorption processes. This study is the first to examine the thermodynamic aspects of pharmaceutical sorption in a fixed-bed soil system, and the findings highlight the method's potential for improving future environmental risk assessments and guiding the development of more accurate contaminant transport models in soils.

1. Introduction

Soils can be conceptualized as complex, multi-phase chromatographic systems interacting with a highly polar mobile phase, the soil solution (Hassett and Banwart, 1989). The sorption mechanisms of pharmaceutically active compounds (PhACs) within this medium are influenced by numerous factors, among them the physicochemical properties of PhACs, the climatic factors (temperature), and the key soil parameters (pH, structure, soil organic matter (SOM)). PhACs sorption, encompassing both adsorption and absorption on the solid phase of soil, which includes mineral surfaces and SOM, is a temperature-dependent process. This sorption may involve specific interactions between polar or charged sites on the soil and polar or charged PhACs molecules, as well as nonspecific interactions between nonpolar sites and nonpolar compounds (Hassett and Banwart, 1989; Milonjic, 2007). In many cases, both types of interactions contribute to the overall process. The sorption of PhACs occurs when the free energy of the sorption reaction (ΔG) is negative (due to contributions from both the enthalpy and entropy

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https://doi.org/10.1016/j.ecoenv.2025.118640

Available online 9 July 2025

terms), signifying that the reaction is thermodynamically favourable and proceeds spontaneously (Hassett and Banwart, 1989; De Oliveira et al., 2017). Therefore, temperature is a very important parameter, as the temperature-dependent viscosity of the soil solution controls mobilisation, immobilisation, and bioavailability (Salvestrini et al., 2020; Maszkowska et al., 2014). When temperature changes in a soil solution system, the mean free path of PhACs may be modified, influencing contact with soil particle surfaces (De Oliveira et al., 2017). The oscillations in temperature, therefore, play a key role in determining the mobilisation and uptake of PhACs by plants (Patel, 2019; Zhang et al., 2014).

While it is crucial to ascertain the thermodynamic characteristics of PhACs in soil colloidal systems, experiments have mostly relied on batch methods (OECD 2000) (No, 2000). Since this technique is simple and inexpensive, some have used it to assess an adsorbate (PhACs) – adsorbent (soil particles) system, making it particularly suitable for examining fundamental physico-chemical interactions (Patel, 2019). Limitations of the batch method include its inability to model soil structure, pore arrangement, and aggregate stability accurately, while also failing to account for the augmentation of spontaneous molecular diffusion by advection currents, leading to intensified mass transfer flux (Thirunavukkarasu et al., 2021). Therefore, if thermodynamic analysis is carried out in a batch system, it is also challenging to derive environmentally relevant thermodynamic parameters. In particular, the most relevant thermodynamic parameters are the standard Gibbs free energy (ΔG^o), which indicates the spontaneity of PhACs sorption processes; the standard entropy change (ΔS^o), which reflects the degree of disorder introduced at the solid–liquid interface; and the standard enthalpy change (ΔH^o), which provides insight into the endothermic or exothermic nature of these interactions (Milonjic, 2007; Ebelegi et al., 2020). This does not yield an ideal representation of a soil system in which liquid can flow or leach out of the soil horizon (Kodešová et al., 2009). In a fixed-bed system, however, thermodynamic parameters can be closer to the actual values when equilibrium is reached, and the cessation of exchange between solid and liquid phases indicates a steady state, allowing for better modeling of soil properties (Doke and Khan, 2013; Imbrogno and Schäfer, 2021; Dubey et al., 2014). A true mass transfer zone of PhACs adsorption may form, behaving like contaminant transport in soil. In a fixed-bed system, it is also possible to model phenomena such as axial dispersion, film diffusion resistance and intra-particle diffusion in soil solutions (Doke and Khan, 2013).

Here, we introduce an unconventional environmental modeling approach that demonstrates how the continuous fixed-bed system provides more accurate thermodynamic and sorption assessments compared to the traditional batch system for soils. Although batch experiments are highly effective in describing molecular-level interactions, they do not directly reveal the relevant chemical behavior in soil environments. Despite the limited number of fixed-bed soil experiments in the literature, it is crucial to expand their application. To address this gap, we compared both techniques, emphasizing that fixed-bed experiments offer a more precise evaluation of the temperature-dependent environmental fate and transport of PhACs in terrestrial systems, providing valuable insights into their realistic behavior.

2. Material and methods

2.1. Soil sampling and characterisation, temperature measurement

Soil samples were collected from the topsoil (0–5 cm) of a carbonate humic sandy soil (Calcaric Humic Arenosol) (representative soils from lowland agricultural regions were chosen for the study) using composite sampling methods (ISO 18400–107:2017) (N47°12'24.3714" E19°40'48.54") (IUSS Working Group WRB, 2022) (Table S1) (Group WRB, (2022)). Temperature variation in the soil was monitored over a complete growing season using PONSEL Odeon combined electrodes (Sigma-Aldrich, USA) (Szalai et al., 2021; Dušek et al., 2008; Vorenhout et al., 2004). Our research group has provided a detailed description of the sampling area in earlier publications (Bell Flow Systems, Buckingham, Great Britain) (Szalai et al., 2021; Szabó et al., 2020, 2024). Following sample collection, soil samples were processed to remove contaminants, standardized for particle size, and analyzed for key physicochemical properties (Szabó et al., 2020, 2024; Filep et al., 2021; Vancsik et al., 2024; Gresina, 2020; Flint and Flint, 2018). Detailed measurements and results on parameters are provided in the supplementary information (Text S1; Table S1). Three PhACs with different physicochemical parameters (17α-ethynylestradiol (EE2), lidocaine-hydrochloride (LID), and diclofenac-sodium (DFC)) were investigated (Table 1). High purity (≥99 %) analytical standards have been purchased from Sigma-Aldrich (USA).

2.2. Experimental setup for adsorption–desorption tests

In this study, two types of experiments were conducted: (1) continuous fixed-bed experiments with single- and trisolution setups across five different temperatures, and (2) batch experiments under the same conditions.

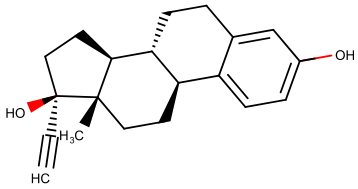
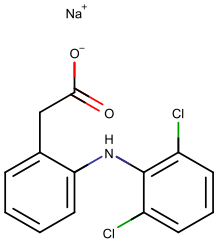
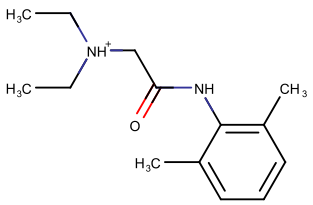
2.2.1. Continous fixed-bed experiments

(1) The separate column fixed-bed experiments were carried out in a borosilicate glass column (ThermoFisher Scientific, USA) (inner diameter = 10 mm) filled with soil (depth = 10 mm) with all experiments conducted in triplicate. Based on preliminary experiments, the mass of the adsorbent was 2 g, due to the enormous sorption capacity of the soil particles in the case of PhACs. Layers of inert glass wool were placed above and below the adsorbent to reduce washout and fringe effects. Flow velocity (downstream flow rate = 2 ml/min) was controlled using a peristaltic pump (LEA BT100F, Lead Fluid (Baoding) Intelligent Equipment Manufacturing Co., Ltd., China). The PhACs were dissolved in 10 ml methanol (Sigma-Aldrich, USA) and 90 ml ultrapure water during the solution preparation process. In all cases, the influent concentration per PhACs in solution was 0.1 μg/ml. The supernatants were passed through a 0.45 μm glass filter (Chromafil® GF/PET-45/25, Sigma-Aldrich, USA) for filtration (Szabó et al., 2024). At pre-defined times, a sample of solution effluent from the column was taken and analysed using a UHPLC (Shimadzu-Nexera X2, Shimadzu, Japan) equipped with a diode array detector (PDA) and a fluorescence detector (FLD) (Table S2). The performance of the fixed bed columns was evaluated through breakthrough curves, where the breakthrough point, at 5 % of initial concentration (C_0), marks the onset of breakthrough, while full saturation is reached when C/C_0 equals one (C refers to the concentration of PhACs in the effluent at any given time during the fixed bed column experiment) (Patel, 2022). At this point, no further exchange between the solid and liquid phases is assumed (Imbrogno and Schäfer, 2021). The experiments involved single and competitive sorption at five different temperatures (278.15 K, 283.15 K, 288.15 K, 293.15 K and 298.15 K) in a climate chamber (ILW 240 STD, Sigma-Aldrich, USA). During both fixed-bed (1) and batch experiments (2), the changes in the pH of the soil solution were continuously monitored, ranging between 7.9 and 8.3 (Sigma-Aldrich, USA). In the single sorption experiments, the mobile phase contained only one PhACs, whereas in the competitive system, it consisted of a tri-solution of PhACs. At each temperature, all experiments were performed in triplicate to ensure reliability and reproducibility. Before the desorption experiment, the column was rinsed with 5 ml of ultrapure water to remove the remained C_0 solution from the system, preventing its influence on the desorption results. The column was flushed with a 0.01 M $CaCl_2$ solution during desorption until reversibly bound PhACs were completely desorbed (Szabó et al., 2020).

2.2.2. Batch experiments

(2) Adsorption and desorption experiments followed the OECD technical guidelines for chemical testing, specifically using a batch

Table 1
Chemical properties calculated for the three pharmaceuticals (EE2, DFC, LID).

		17α-ethynylestradiol (EE2)	Diclofenac-sodium (DFC)	Lidocaine hydrochloride (LID)
Structure				
logD		3.88	0.76	2.80
Microspecies distributions % at	α_0[a]	97	0	90
pH 7.9	α_+[b]	0	0	10
	α_-[c]	3	100	0
nHBd[d]		1.97	1	1.1
nHBa[e]		4.03	6	2.9
π energy		18.5	31.6	17.6
Aromaticity %		13	40	15
Van der Waals surface area		460.4	359.6	426.0

[a] fraction of PhACs as neutral form;
[b] fraction of PhACs as positive form;
[c] fraction of PhACs as negative form;
[d] the number of hydrogen bond donor sites;
[e] the number of hydrogen bond acceptor sites. The physicochemical parameters of the PhACss were calculated using MarvinSketch by Chemaxon.

equilibrium approach (No, 2000; Szabó et al., 2020, 2024). The sorption of the three PhACs was conducted in darkness at the same constant temperatures as the fixed-bed experiments in an incubator. The adsorption kinetic studies had already been conducted according to the same standard, confirming that a 24-hour equilibrium time was sufficient for the adsorption of all PhACs. However, for DFC and LID, equilibrium was reached within just one hour, whereas EE2 required the full 24-hour period to achieve equilibrium [16,20]. Based on preliminary tests, the soil-to-solution ratio was set to 1:12. The soil solution in Falcon tubes (ThermoFisher Scientific, USA) were agitated on a mechanical round shaker (ThermoFisher Scientific, USA) (Szabó et al., 2020, 2024). Simultaneously, blank samples were also prepared and analyzed, confirming no PhACs presence in the soil and no degradation under blank conditions. In previous studies, we confirmed that the soil samples were free from PhACs; however, to ensure accuracy, we also analyzed a blank soil sample as a control (Szalai et al., 2021; Szabó et al., 2024). Prior to analysis, samples were centrifuged at 5200 rpm for 15 min (MPW-352RH Sigma-Aldrich, USA).

Following adsorption, 0.01 M $CaCl_2$ solution was added to each soil sample, and the Falcon tubes were shaken for another 24 h (Szabó et al., 2020, 2024). This same protocol was applied to both the desorption and adsorption steps, with the desorption process repeated three times over a total of 144 h. Measurements included both single- and multicomponent setups. In the ternary competitive setup, all three PhACs were added simultaneously in equal ratios. Concentrations for each PhACs were kept consistent with those used in the fixed-bed experiments, and stock solutions were diluted with methanol. Sodium azide (0.1 g) (Sigma-Aldrich, USA) was added to each solution during measurements to prevent PhACs degradation against microbiological activites (Vancsik et al., 2024).

2.3. Modeling and data evaluation

2.3.1. Sorption and thermodynamic parameter estimation

To characterize the thermodynamics of PhACs soprtion on soil, we calculated thermodynamic and sorption parameters, including the amount of PhACs adsorbed onto the soil's surface at a specific time point ti (q_{ti}; μg/g) [20], K_d [22], K_c [2,12], ΔG^0 (kJ/mol) [1], ΔH^0 (kJ/mol) [Hassett and Banwart, 2015], ΔS^0 (kJ/mol)[2], maximum saturated amount (q_{max}; μg/g), adsorption area (Aa; min), breakthrough time (T_{break}), saturation time (T_{sat}), size of the mass transfer zone (MTZ; mm), total bed desorption capacity (qd_{total}; μg), bed desorption capacity (q_{dbed}; μg/g), desorption percentage (*D%*) (Table 1; Text S2).

2.4. Statistical and chemometric analysis

Temperature-dependent variance components were identified using Principal Component Analysis (PCA). Normality of distributions was assessed with the Shapiro-Wilk and Lillieforst tests, and Pearson's correlation coefficient was used to evaluate linear associations between variables, with ordinary least squares regression modeling relationships and fit (Text S3). All parameters were computed in R Studio and Origin 2020 software. Detailed calculations and methodologies are provided in the supporting information (Text S2;Text S3).

3. Results and discussion

3.1. Monitoring of soil temperature fluctuations

In agricultural areas, the abundance of PhACs is high during the growing season, prompting our incorporation of temperature parameters in the sorption modelling (Nguyen et al., 2023). Topsoil temperatures vary between 282.38 K in early April and 292.70 K in late September (Fig. 1). These variations illustrate that upper soil temperatures can vary significantly within a single day. On April 2, 2023 (early stage of the vegetation period), temperatures ranged from a minimum of 283.67 K to a maximum of 286.65 K. On August 2, 2023 (middle of the growing season), they fluctuated between 288.23 K and 292.09 K, while on September 15, 2023 (end of the vegetation period), temperatures spanned from 285.98 K to 288.42 K. Such rapid daily micro-changes in temperature are crucial in determining whether PhACs adsorb in the root zone, remain in the liquid phase, or undergo desorption and become more mobile. PhACs that have been persistently adsorbed in the topsoil during the growing season may also be affected by larger temperature fluctuations beyond the season (e.g. winter period).

Table 2
Key Equations Applied in Sorption Modelling and Thermodynamic Evaluation.

Type	Operators	Equations	Parameters
Sorption	q_{ti}	$(C_0 - C_e)\frac{V}{m}$	$\boldsymbol{q_{ti}}$ - the amount of PhACs adsorbed onto the soil's surface at a specific time point t_i (in μg/g) $\boldsymbol{C_0}$ - the initial concentration of PhACs in the solution (μg/L) $\boldsymbol{C_e}$ - the concentration of PhACs remaining in solution at time ti (μg/L) $\boldsymbol{V}$ - the volume of the soil solution used in the experiment (L) $\boldsymbol{m}$ - the mass of the soil (g)
	K_d	$\frac{q_{ti}}{C_e}$	$\mathbf{K_d}$ - the non-dimensionless linear distribution coefficient (dm^3/g) $\boldsymbol{q_{ti}}$, $\boldsymbol{C_e}$
	K_C	$K_d \bullet 1000$	$\mathbf{K_C}$ - dimensionless linear distribution coefficient $\mathbf{K_d}$
	$q_{\max}$	$\sum q_{ti}$	$\boldsymbol{q_{max}}$ - the maximum saturated amount (μg/g) $\boldsymbol{q_{ti}}$
	Aa	*Trapezoidal rule of integration*	$\boldsymbol{Aa}$ - the adsorption area (min)
	T_{break}	$C_0 * 0.05$	$\mathbf{T_{break}}$ - the breakthrough time (min) $\boldsymbol{C_0}$
	T_{sat}	$C_t = C_0$	$\boldsymbol{T_{sat}}$ - saturation time (min) $\boldsymbol{C_t}$ - the concentration of PhACs in the effluent at any given time during the fixed bed column experiment (μg/L)
	MTZ	$Z \bullet (1 - \frac{T_{break}}{T_{sat}})$	$\boldsymbol{MTZ}$ -the size of the mass transfer zone (mm) $\boldsymbol{Z}$ - the column height (mm)
	q_{dtotal}	$Q \bullet Da$	$\boldsymbol{q_{dtotal}}$ - the total bed desorption capacity (μg) $\boldsymbol{Q}$ - the feed flow rate (ml/min) **Da** - the area under the experimental desorption curve (min) (composite trapezoidal rule)
	q_{dbed}	$q_{dtotal} \bullet m$	$\boldsymbol{q_{dbed}}$- the bed desorption capacity (μg/g) $\boldsymbol{q_{dtotal}}$, $\boldsymbol{m}$
	D%	$\frac{\sum dq_{ti}}{q_{\max}} \bullet 100$	$\boldsymbol{D}$% - the desorption percentage (%) $\boldsymbol{dq_{ti}}$- the quantity of PhAC released from the soil surface at a specific time point, ti (μg/g)
Thermodynamics	ΔG^0	$-RT\ln K_C$	$\boldsymbol{\Delta G^0}$ - the standard Gibbs' free energy (J/mol) $\boldsymbol{R}$ - the universal gas constant (J/mol·K) $\boldsymbol{T}$ - the temperature (K) $\mathbf{K_C}$
	ΔG^0	$\Delta H^0 - T\Delta S^0$	$\boldsymbol{\Delta H^0}$ - the standard enthalpy change (J/mol) $\boldsymbol{\Delta S^0}$ - the standard entropy change (J/mol) $\boldsymbol{\Delta G^0}$, $\boldsymbol{T}$
	$\ln K_C$	$\frac{\Delta S^0}{R} - \left(\frac{\Delta H^0}{R}\right)\left(\frac{1}{T}\right)$	$\mathbf{K_C}$, $\boldsymbol{\Delta S^0}$, $\boldsymbol{R}$, $\boldsymbol{\Delta H^0}$, $\boldsymbol{T}$

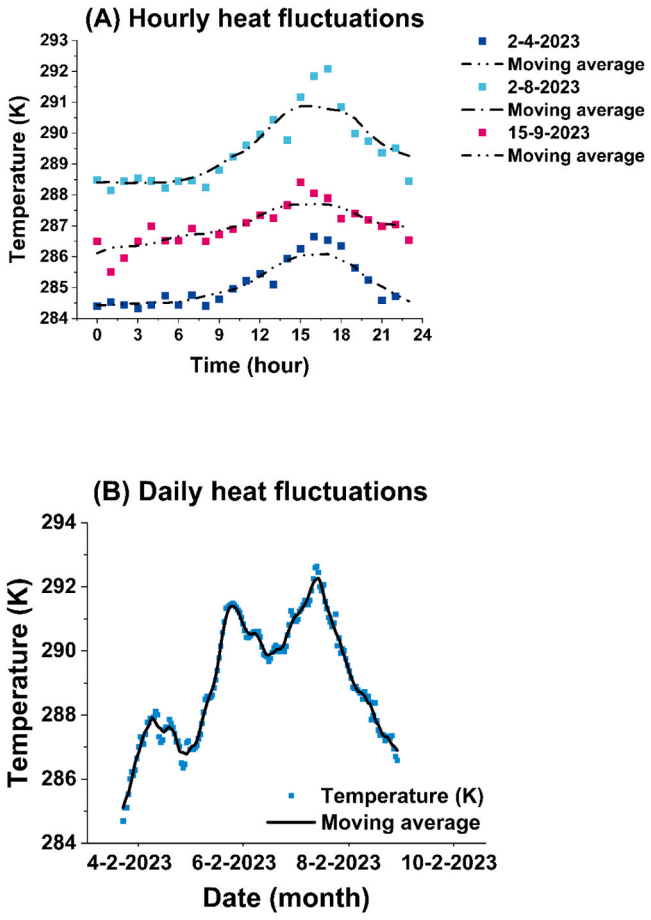


Fig. 1. (A) Hourly soil temperature variations (in Kelvin) on selected days within the vegetation period (April 2, 2023; August 2, 2023; and September 15, 2023–3-day moving average). (B) Daily soil temperature variations measured at 12:00 pm throughout the vegetation period (in Kelvin) for the sampled area.

3.2. Sorption behaviour in the light of temperature changes in a fixed-bed system

The temperature and synergistic effects are also reflected in the sorption data (Szabó et al., 2024; Al-Khateeb et al., 2014; Kodešová et al., 2023). For EE2 in a single system, the adsorbed amount increased as the temperature rose (e.g. 2.77 ± 0.02 μg/g → 4.79 ± 0.03 μg/g), and the saturation time also increased proportionally (Figure S1, Table S3). In the competitive system, it showed the opposite dynamic. As the temperature rose, the adsorbed amount decreased (e.g. 2.82 ± 0.4 μg/g → 1.36 ± 0.3 μg/g), and the soil column became saturated in a shorter time (Fig. 2, Table S4) (Qin et al., 2017). Desorption data show the same inverse trend between the two sorption systems. In the single system, the desorbed amount decreased with increasing temperature. However, in the competitive system, it increased, resulting in the total desorbed amount being released from the soil at 298.15 K (Table S5).

The LID tendency in the single system was similar to that of EE2 (Table S3), whereas in the competitive system, the adsorbed amount increased from 278.15 K (0.52 ± 0.00 μg/g) to 288.15 K (0.74 ± 0.2 μg/g) (Table S4, Fig. 2). The temperature optimum for LID adsorption was ~288.15 K, below and above which both adsorption and saturation time decreased. Desorption was minimal in both systems for LID, indicating that it adsorbed irreversibly (Table S5). Due to the dissociation of LID, ionic interactions with the charged surfaces of the SOM are assumed, which may cause irreversibility. In a single system, the extent of adsorption for DFC increased, while the desorbed amount decreased with rising temperature (Table S5). However, in the trisolute/

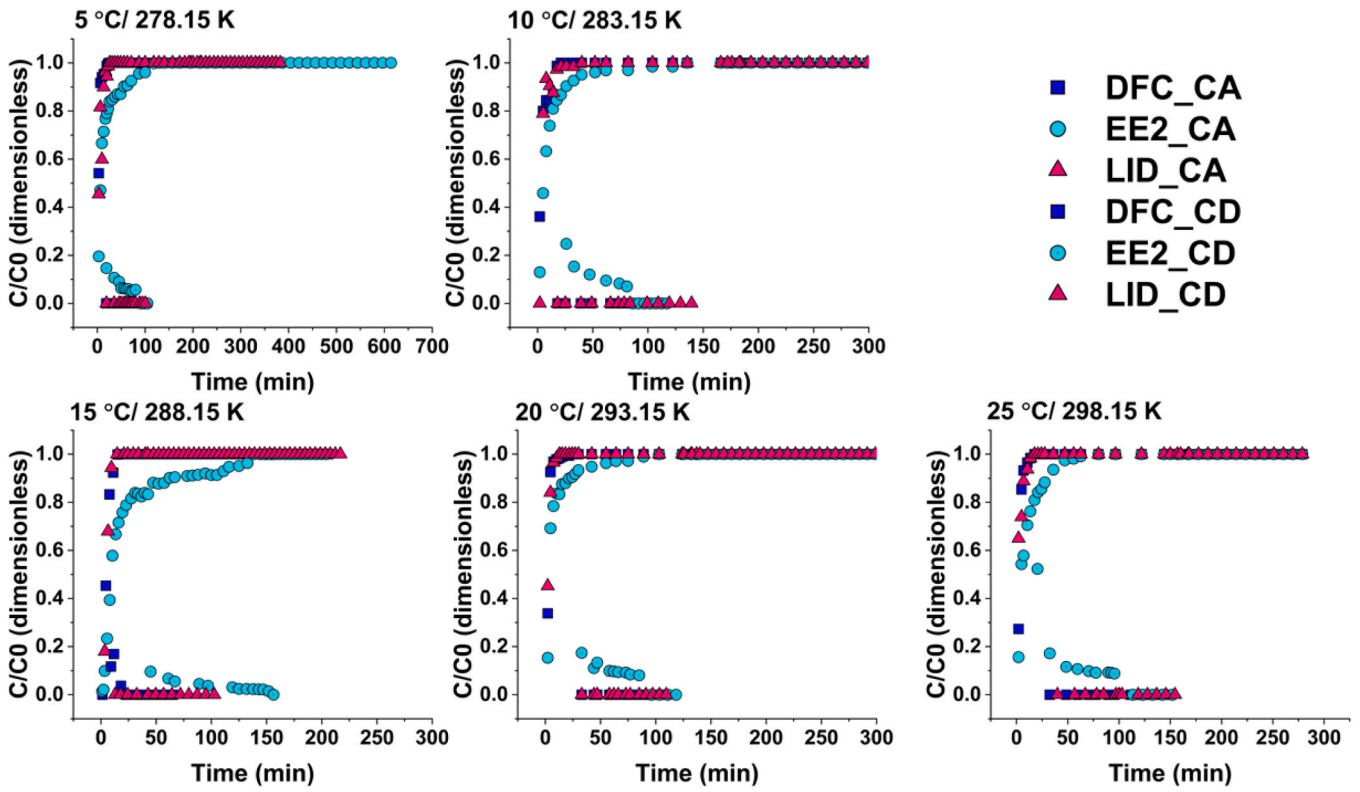


Fig. 2. Breakthrough Curves for competitive Adsorption/Desorption Processes of PhACs (this figure presents breakthrough curves illustrating the adsorption and desorption behaviours of PhACs— EE2 =17α-ethynylestradiol, LID=lidocaine-hydrochloride, and diclofenac-sodium (DFC)—in multicomponent (CA: adsorption, CD: desorption) systems. The y-axis represents the normalized concentration ratio (C/C_0), indicating the concentration of PhACs in the effluent relative to the initial concentration. The x-axis shows elapsed time, capturing the progression of adsorption and desorption processes.

competitive system, as in the cases of LID, the adsorption has an optimal temperature. The highest adsorption of DFC occurred at ~288.15 K (0.72 ± 0.02 μg/g), decreasing as the temperature varied. The adsorbed amounts were irreversible under all conditions.

PhACs essentially co-occur in environmental systems so that the environmental relevance can be predicted primarily from the results of the multi-component system. The environmental implication is that EE2 is more likely to bind irreversibly at colder temperatures (the beginning and the end of the growing season, the morning and evening temperatures (Yacoubi et al., 2010)) than higher temperatures. As the summer warm-up and daily soil temperatures rise, all adsorbed EE2 can be released. As a result of temperature fluctuations, EE2 may be available for nutrient uptake (absorption by roots) by crops during the day section (Carter et al., 2014). The adsorption optimum for DFC and LID is around 288.15 K, the base temperature for the morning and evening of the summer period, when irrigation is practiced (Yacoubi et al., 2010) (Fig. 1). Agricultural land is usually irrigated in the morning and evening hours to reduce evaporation losses, so it is important to consider changes in soil temperature during the growing season due to the terrestrial transport of organic micropollutants (Yacoubi et al., 2010). Although solar heat fluxes can be high, it is important to consider that soil temperature is a less dynamically variable system.

3.3. *Thermodynamic and sorption parameters in batch and fixed-bed systems*

In evaluating the thermodynamic and sorption behavior of PhACs, both batch and fixed-bed systems provided a range of insights into how temperature affects adsorption and desorption dynamics in soil-liquid environments. The fixed-bed system, which more closely mimics natural soil conditions, allowed for a detailed examination of the temperature-dependent interactions between PhACs and soil particles. Key thermodynamic parameters, ΔG^0, q_{max} and q_{dtotal}, were analyzed to understand how these systems behave under varying thermal conditions.

ΔG^0 that best expresses the strong inverse (-0.95) correlation between temperature variation and q_{max} (Fig. 3). In batch systems, no correlation (-0.29) is observed between these parameters, indicating that fixed-bed systems offer better insights into the thermodynamic behaviour of PhACs in soil-liquid systems. The same trend appears for ΔG^0 and q_{dtotal}, suggesting that there is also an inverse relationship (-0.72) between desorption and ΔG^0, something not apparent in the results of the batch experiment (Figure S3). As a fixed-bed system describes more precisely the actual environmental conditions, such as soil permeability, natural saturation, contact time, axial and intra-particular dispersion, thermodynamic analyses are more accurate for PhACs-soil particle interaction. Despite not being a conventional approach in soil science, column experiments may provide a more realistic assessment of sorption processes, and their broader application should be considered. To facilitate this, developing a standardized methodology similar to the OECD guidelines could help establish fixed-bed systems as a reliable tool for evaluating the environmental fate of organic contaminants in soils.

Thermodynamic equilibrium is assumed when the mass transfer zone has passed through the whole column (fully saturated) (Imbrogno and Schäfer, 2021; Ivanković et al., 2021). The K_C, q_e, ΔG^0, ΔS^0, ΔH^0 were calculated at the moment of equilibrium (Table S6, Table S7). For all PhACs at all temperatures, ΔG^0 is negative, meaning the stability of the soil particle – PhACs interaction is more robust than that of the soil solution – soil particle interaction (Bernal et al., 2021) (Table S6). Negative ΔG^0 parameters indicate that all sorption was a spontaneous process. In single- and multicomponent systems, the decreasing ΔG^0 value of DFC, and in single-system LID and EE2 with rising temperature, suggests a significant increase in the adsorption affinity of PhACs, implying higher soil adsorption capacity. In a competitive system, the

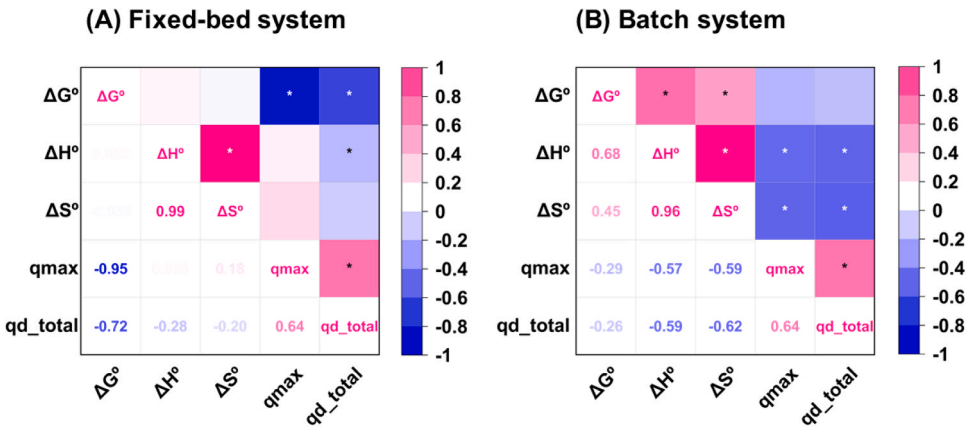


Fig. 3. Pearson correlation between key sorption and thermodynamic parameters following experiments in (A) the fixed-bed system and (B) the batch system. Crosses indicate significant correlations at the 0.05 significance level (2-tailed).

increasing ΔG^0 values of LID and EE2 with temperature indicate less spontaneity, implying a decrease in adsorption affinity Jain et al., (2014). Several PhACs can be present in a soil-solution system simultaneously, so in the warmer part of the growing season, increased DFC adsorption can be expected, with a decrease for LID and EE2 (Fig. 4).

In soil-colloid systems, the primary enthalpy-based adsorption forces between PhACs and soil particles include London-van der Waals forces (arising from temporary dipoles created by small electron shifts), Coulomb electrostatic interactions and charge transfer complexes between electron donor and acceptor molecules, π-bonding interactions due to overlapping bond trajectories perpendicular to the aromatic rings, and hydrogen bonding, where a hydrogen atom forms a bridge between molecules, typically as an induced dipole effect, further stabilising PhACs-soil interactions[1]. ΔH^0 data help differentiate between physical and chemical adsorption. Chemisorption (a first-order chemical bond can be formed between PhACs and surface atoms of the soil solid phase) typically shows enthalpy changes $\Delta H^0 > 60$ kJ/mol, while physisorption (above mentioned secondary interections) is $\Delta H^0 < 40$ kJ/mol (Feng et al., 2010). ΔH^0 suggests that the intermolecular interactions between soil particles and PhACs represent physisorption since the adsorption energies are below 40 kJ/mol. The mean ΔH^0 of all PhACs was positive, suggesting that the adsorption processes were endothermic. ΔH^0 values signalled that the system was absorbing energy from the environment to disrupt adsorbent-solvent interactions (Al-Khateeb et al., 2014; Bernal et al., 2021; Feng et al., 2010). The sorption of PhACs in soil is influenced by the relative binding forces (ΔH^0) between the PhACs and soil particles compared to those in the surrounding solvent (Hassett and Banwart, 1989). The ΔH° value of DFC in the competitive system was similar to that in the single system. However, EE2 and LID exhibited negative ΔH° values in the competitive system, in contrast to the single-component case, where the enthalpy change was positive or close to zero. This indicates that the adsorption of EE2 and LID became exothermic in the presence of competing compounds, suggesting a shift in the sorption mechanism or a change in the

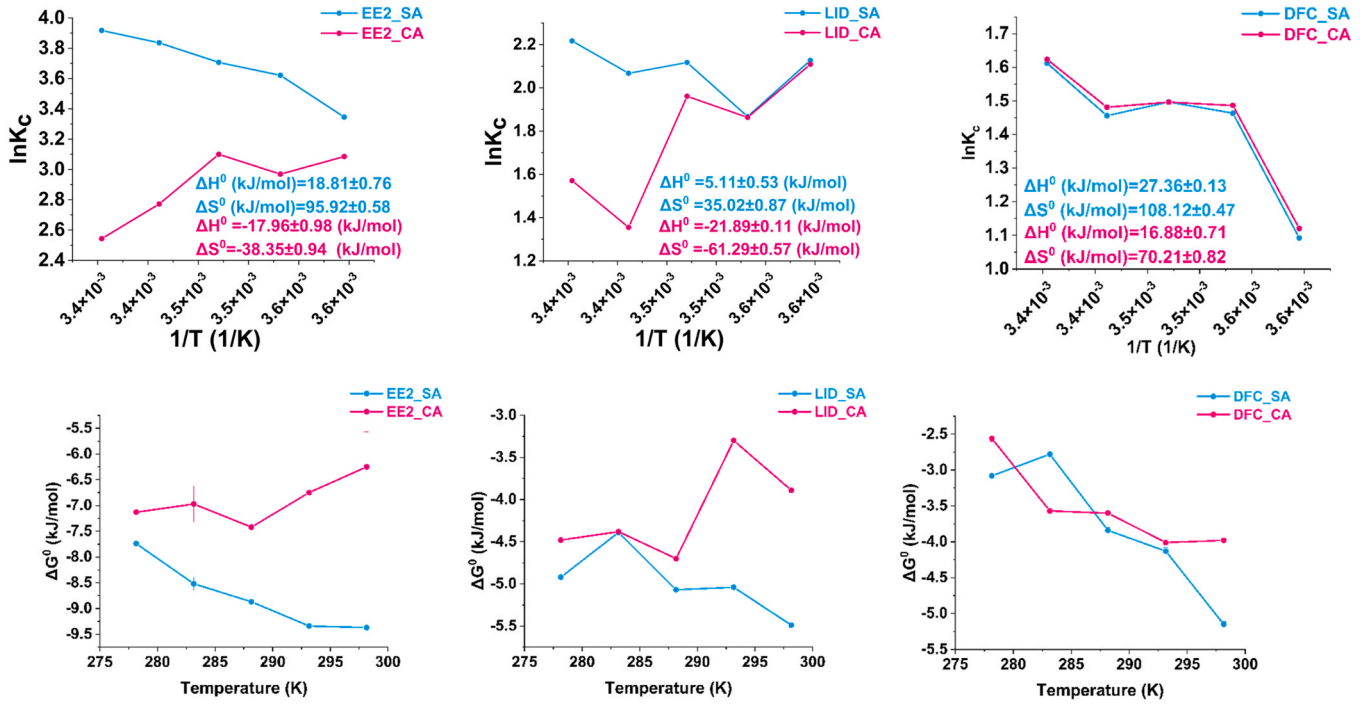


Fig. 4. Van't Hoff plot illustrating the relationship between $\ln K_c$ and 1/T (linear correlation derived from the Van't Hoff equation, where the slope ($-\Delta H^0/R$) and the intercept ($\Delta S^0/R$) enable the determination of ΔH^0 and ΔS^0). Temperature dependence of ΔG^0 values in the fixed-bed system for single (green(SA)) and competitive (pink(CA)) setups: 17α-ethynylestradiol (EE2), lidocaine hydrochloride (LID), and diclofenac sodium (DFC).

interaction energy with soil particles. The release of energy implies that physical adsorption processes dominated, such as London dispersion forces, π–π interactions, Coulombic attraction, or charge transfer.

The ΔS^0 of PhACs was positive, suggesting an increase in randomness at the solid-liquid interface, leading to an increase in the degree of freedom of the PhACs (Suriyanon et al., 2013; Lonappan et al., 2018). The adsorbed solvent molecules displaced by the adsorbed PhACs gain greater translational randomness in the system. Additionally, changes in system disorder (ΔS^0) play a role, where increased randomness generally favors the sorption process (Hassett and Banwart, 1989). A positive ΔS^0 reflects the affinity of the adsorbent for the adsorbed species and indicates an increase in solid-solute randomness. Entropy-driven chemical interactions in soils, such as hydrophobic interactions, occur between PhACs and soil particles. In these processes, organic compounds transition from the polar aqueous phase to hydrophobic surfaces within the soil (Hassett and Banwart, 1989; Salvestrini et al., 2020). The ΔS^0 values of DFC were similar (just like ΔH^0) in the competitive system. Variation in the ΔS^0 of EE2 and LID was the opposite. The negative value of ΔS^0 indicated that randomness at the solid-solution interface decreased during the immobilisation (reduction in the degree of freedom at the solid-liquid interface) when temperature increased (Al-Khateeb et al., 2014). A negative ΔS^0 also indicates a decrease in the disorder of the solid-liquid interface during adsorption, implying an enhanced migration of PhACs from solid to liquid phases. When both LID and EE2 display negative ΔS^0 values, this indicates a decrease in affinity for soil particles compared to a single system (ΔH^0, ΔG^0 same trend, correlated with q_{max} values). These phenomena suggest an antagonistic effect where they displace each other from adsorption sites. It therefore follows that their endothermic ($\Delta H^0>0$) reactions in a single system become exothermic ($\Delta H^0<0$) in a multicomponent system, as competition leads to the availability of lower-energy adsorption sites, reducing the need for energy absorption from the environment, thus decreasing adsorption affinity.

Summing up, temperature-dependent sorption processes were observed, revealing that DFC exhibits increased adsorption at higher temperatures, while the adsorption of LID and EE2 decreases in a multicomponent system. As the growing season progresses, the highest adsorption of DFC can be expected in the middle of the season, when the average temperature is highest. Conversely, during the initial and final stages of the growing season and in the morning and evening when temperatures are comparatively lower, an enhancement in LID and EE2 adsorption is anticipated in irrigated ploughed soil. The physical nature of the sorption process of PhACs indicates weak bonding forces, e.g. hydrogen bonds and London van der Waals interactions. These physical bonds thus suggest that the PhACs examined are more readily mobilised in the soil than through stronger ionic interactions. The pH was monitored throughout the experiments, with values ranging from 7.9 to 8.3. This pH fluctuation had a direct impact on the dissociation of LID. As the pH level increased, the percentage of LID that remained uncharged also increased. In the case of LID, the focus can be shifted to hydrophobic interactions.

3.4. Relationship among intrinsic properties of PhACs and thermodynamic parameters in fixed-bed systems

PhACs with different physicochemical properties are significantly separated in the PCA ordination space. The loadings of EE2 tend towards the positive factors in PC_1. An inverse relationship was found between ΔG^0, a negative factor loading in PC_1, and the positive adsorption parameters, suggesting that the adsorption affinity of PhACs in soils may be most strongly determined by the temperature-derived ΔG^0. This is confirmed by the linear regression (r^2=0.902) between the q_{max} of the soil particle and ΔG^0. The adsorption affinities of PhACs increase significantly with temperature in a single system (e.g. EE2, q_{max}: from 2.77 μg/g to 4.79 μg/g) (Fig. 5; Table 3, Table S3). The linear relationship between q_{max} and ΔG^0 remains, but the direction of the relationship has shifted in the multicomponent system for LID and EE2

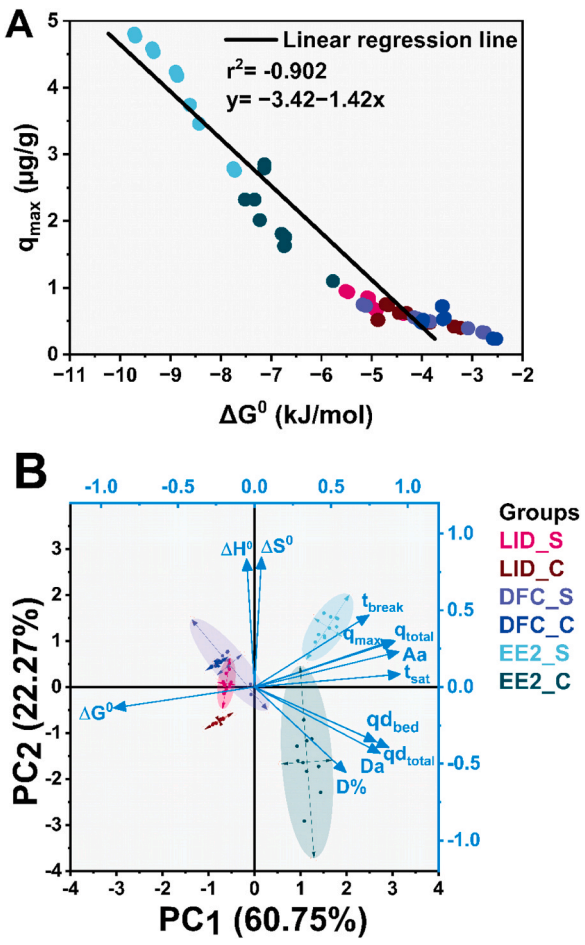


Fig. 5. (A) Linear regression between maximum saturated amount (q_{max}) and Gibbs free energy ΔG^0, with the regression equation and r^2 value provided to represent the strength of the relationship. (B) Ordination space from the principal component analysis. Labels indicate different PhACs setups: LID_S represents lidocaine-hydrochloride in the single system, LID_C represents lidocaine-hydrochloride in the competitive system, DFC_S denotes diclofenac-sodium in the single system, DFC_C denotes diclofenac-sodium in the competitive system, EE2_S denotes 17α-ethynylestradiol in the single system, and EE2_C denotes 17α-ethynylestradiol in the competitive system.

Table 3
Results of principal component analysis for the fixed-bed sorption parameters with rotated factor weights, highlighting weights greater than 0.8.

Parameters	Principal components	
	PC_1	PC_2
ΔG^0	**−0.919**	−0.137
ΔH^0	−0.051	**0.835**
ΔS^0	0.046	**0.846**
t_{break}	0.747	0.469
t_{sat}	**0.951**	0.084
q_{max}	**0.906**	0.304
Aa	**0.942**	0.230
q_{total}	**0.917**	0.298
Da	**0.819**	−0.432
q_{dtotal}	**0.877**	−0.395
q_{dbed}	0.795	−0.357
D%	0.597	−0.557

The observed sorption behaviour of PhACs in the fixed-bed system can be partly explained by their molecular descriptors, such as logD, π-energy, aromaticity, and dissociation state at the working pH. These

properties directly affect how each compound interacts with the aqueous phase and the soil's organic and mineral surfaces. EE2, with its high logD (3.88) and moderate π-energy (18.5), shows strong hydrophobic interactions with SOM, which explains its higher mobility and increased desorption at elevated temperatures (Szabó et al., 2020, 2024). In contrast, the irreversible retention of LID and DFC can be attributed to their ionic forms under experimental pH conditions: LID is predominantly positively charged, while DFC is fully anionic, promoting electrostatic interactions with oppositely charged sites on the soil matrix (Szabó et al., 2024; Filep et al., 2021). Additionally, DFC exhibits the highest π-energy (31.6) and aromaticity (40 %) among the studied compounds, enabling strong π–π interactions with aromatic domains in soil organic matter (Szabó et al., 2020, 2024; Filep et al., 2021). These interactions are typically associated with more stable and less reversible adsorption. Consequently, such compound-specific interactions help to explain the variability in thermodynamic parameters such as ΔH^o, ΔS^o, and ΔG^o. This highlights the importance of integrating molecular descriptors into fixed-bed sorption modelling to more accurately predict the environmental behaviour of PhACs in soil systems.

Desorption is also controlled by temperature in the PCA ordination space and desorption parameters are opposite to ΔG^0. For hydrophobic EE2, when the temperature increased (negative correlation between ΔG^0 and q_{dtotal}) there was great desorption activity (Table S5). In the multicomponent system, desorption was higher at all temperatures, explained by the compositional interaction of compounds and fewer potential adsorption sites (Szabó et al., 2020; Filep et al., 2021). LID and DFC binding was completely irreversible in the competitive system, while in the single, desorption was reversible at lower temperatures, only becoming irreversible at higher temperatures. This implies that if an intraday temperature change occurs, irreversible desorption becomes reversible, and is available again during nutrient uptake by crops (Vancsik et al., 2024; Carter et al., 2014; Christou et al., 2017).

4. Conclusion

Daily micro-changes in temperature over the growing season can significantly affect the residence time of PhACs in the root zone. Field measurements indicate that soil temperature fluctuates significantly throughout the year, meaning that PhACs adsorbed in the root zone during the vegetation period may undergo desorption under different thermodynamic conditions later in the year. In colder periods, these changes can alter their sorption activity, potentially influencing their mobility and availability in the soil environment. This can completely rewrite the bioavailability of PhACs in the soil-solutions system. An accurate estimating method for the thermodynamic behaviour of PhACs in soils is therefore required. The statistical analysis here demonstrates the greater effectiveness of fixed bed systems (with the correct K_c value) in investigating thermodynamic properties, as ΔG^0 values (the basis of all other thermodynamic parameters) showed a strong correlation and regression with maximum saturated amount (q_{max}) and total desorption (q_{dtotal}). These results show that the sorption processes of PhACs are temperature-dependent physical phenomena (e.g. hydrogen bonds and London dispersion forces), while ion exchange sorption may also play a role in their retention within the soil matrix. PhACs can become mobile or be adsorbed onto the soil particles due to sudden temperature changes (e.g. EE2 in a single system, temperature from 278.15 K to 298.15 K, q_{max} from 2.77 μg/g to 4.79 μg/g). Additionally, PhACs that were adsorbed during the vegetation period may undergo desorption in a different season as a result of temperature variations. From an environmental perspective, during the times when agricultural land is irrigated—typically in the cooler periods of the morning and evening—there is an increased adsorption of the tested PhACs. As daytime temperatures rise, we can expect that EE2 will gradually desorb from the soil particles, while soil particles will fully retain DFC and LID. This new methodology (in soil science), incorporating negative correlations, accurately predicts PhACs sorption in fixed-bed systems, surpassing batch methods in correlating adsorption-desorption and thermodynamic data. We emphasize that this rarely used approach provides a better view of the temperature-dependent fate of organic soil pollutants. While fixed-bed systems are commonly applied in industrial filtration processes, we also recommend their use for soil studies to achieve a more precise environmental reconstruction. Implementing fixed-bed systems in soil chemistry allows for a more accurate assessment of the environmental fate of PhACs, improving our understanding of their long-term behavior in terrestrial ecosystems.

Associated Content

None

Supporting Information

The Supporting Information is available free of charge.

CRediT authorship contribution statement

Anna Vancsik: Visualization. **Zoltán Szalai:** Writing – original draft, Funding acquisition, Conceptualization. **László Bauer:** Writing – original draft, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Szabo Lili:** Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Bruna Silva:** Data curation. **Zoltán Dévény:** Visualization. **Attila Csaba Kondor:** Writing – review & editing, Funding acquisition.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors have not used any AI or AI-assisted technologies.

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.

Acknowledgements

This research was supported by OTKA K142865 (Zoltán Szalai), NKFIH 2020–1.1.2-PIACI-KFI-2021–00309 (Attila Csaba Kondor); 2021–1.2.4-TÉT-2021–00029 (Attila Csaba Kondor), DKOP-23_3 (László Bauer),. and KDP-24-II-ELTE-19 (Zoltán Dévény)

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2025.118640.

Data availability

Data will be made available on request.

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