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Impact of Temperature Variation on the Sorption Kinetics and Mobility of Pentachlorophenol in Organic-Rich Soils

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Abstract

The environmental fate of persistent organic pollutants such as pentachlorophenol (PCP) is governed by their interaction with soil matrices under variable thermal conditions. Understanding how temperature influences sorption and desorption kinetics is critical for predicting contaminant mobility, bioavailability, and long-term ecological risk. This study investigates the impact of temperature variation on the sorption kinetics and mobility of pentachlorophenol in organic-rich soils, providing insight into thermally driven transport processes relevant to climate change scenarios. Experiments were conducted across a range of controlled temperatures to evaluate changes in sorption equilibrium, rate constants, and desorption hysteresis. Results indicated that increasing temperature reduced overall sorption capacity, reflecting a shift from chemisorption-dominated mechanisms to more reversible physical adsorption. Activation energy calculations suggested that sorption was an exothermic process influenced by soil organic matter composition and micropore accessibility. Desorption studies revealed enhanced PCP release at higher temperatures, implying greater mobility and potential for groundwater contamination under warming conditions. Kinetic modeling using pseudo-first-order and pseudo-second-order equations demonstrated that temperature modulated both adsorption affinity and desorption rate constants, aligning with the Arrhenius and Van't Hoff relationships. These findings underscore the sensitivity of contaminant-soil interactions to climatic variations, particularly in organic-rich environments where sorption equilibria govern pollutant persistence. The study contributes to predictive frameworks for environmental risk assessment by integrating thermodynamic parameters with sorption kinetics, supporting more accurate modeling of pollutant migration in changing climatic contexts. Ultimately, this work highlights the necessity of incorporating temperature-dependent sorption behavior into contaminant transport models to guide remediation strategies and regulatory policies for persistent organic pollutants.

Keywords: Pentachlorophenol; Sorption kinetics; Temperature variation; Organic-rich soils; Contaminant mobility; Climate change

1. Introduction

Persistent Organic Pollutants (POPs) represent a major environmental challenge due to their toxicity, longevity, and tendency to bioaccumulate across trophic levels [1]. Among them, pentachlorophenol (PCP) has gained considerable attention as a model compound for studying the environmental persistence of chlorinated phenols used in wood preservation, pesticide formulations, and industrial biocides [2]. Its aromatic ring structure, chlorination pattern, and hydrophobicity confer high chemical stability, allowing it to resist microbial degradation and persist in terrestrial and aquatic ecosystems [3]. Once introduced into soils, PCP can partition between solid and aqueous phases, bind to organic matter, and undergo complex sorption–desorption interactions that dictate its environmental fate [4].

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The sorption behavior of PCP in soils is primarily influenced by soil organic matter (SOM) content, mineral composition, and physicochemical conditions such as pH and temperature [5]. Organic-rich soils, characterized by high humic and fulvic acid concentrations, often display strong affinity for PCP through hydrogen bonding, π–π interactions, and hydrophobic partitioning mechanisms [6]. However, desorption processes can gradually release bound PCP back into the soil solution, facilitating its mobility and potential groundwater contamination [7]. These reversible interactions highlight the dynamic nature of PCP–soil equilibria, where small environmental perturbations can significantly alter contaminant transport patterns [8].

Temperature variation is one of the most critical yet underexplored factors controlling sorption dynamics. Changes in thermal energy can influence diffusion rates, adsorption affinities, and desorption kinetics, ultimately determining contaminant persistence and migration potential [9]. In warmer conditions, enhanced molecular motion can reduce sorption strength, leading to increased mobility, while cooler environments may stabilize soil–solute interactions. Understanding these temperature-dependent mechanisms is therefore essential for predicting contaminant behavior under evolving climatic scenarios and for designing effective remediation strategies that consider thermal variability as a governing factor in contaminant fate modeling.

Recognizing the significance of temperature on PCP sorption behavior underscores the need for systematic kinetic and thermodynamic analyses to predict pollutant fate under shifting environmental conditions.

1.1. Research Problem and Objectives

Despite extensive research on the adsorption of organic contaminants, there remains a lack of quantitative understanding regarding how temperature modulates PCP sorption kinetics and mobility in organic-rich soils [4]. Previous studies have primarily focused on equilibrium modeling under constant laboratory temperatures, neglecting the dynamic fluctuations that occur in natural settings [1]. Moreover, while thermodynamic investigations have reported exothermic tendencies of PCP adsorption, the interplay between kinetic control and thermal energy remains insufficiently characterized [6]. Such knowledge gaps hinder the accurate extrapolation of laboratory results to field-scale contaminant transport models.

The present investigation aims to address these deficiencies by systematically examining how varying temperature conditions influence both the sorption and desorption kinetics of PCP in organic-rich soils [8]. The research focuses on identifying temperature thresholds that govern the transition between physical and chemical adsorption processes, providing deeper insight into contaminant–soil interactions. Specifically, the objectives are threefold:

(i) To determine the sorption and desorption kinetics of PCP under variable temperature conditions, quantifying how adsorption rate constants, equilibrium times, and desorption capacities shift across a defined thermal gradient [3].

(ii) To evaluate thermodynamic parameters, including enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°), in order to distinguish between spontaneous and non-spontaneous sorption mechanisms, and to assess the energetic favorability of temperature-dependent processes [2].

(iii) To interpret the mechanistic implications of these findings for contaminant mobility and soil–water partitioning, linking laboratory observations to environmental risk assessments and pollutant transport predictions in natural soils [5].

By integrating kinetic, thermodynamic, and mechanistic approaches, this study seeks to provide a comprehensive understanding of how temperature governs the sorption equilibria of PCP in organic-rich matrices [9]. The results are expected to contribute valuable parameters for predictive modeling and risk evaluation, particularly under climate-induced temperature variations that affect pollutant dynamics. Upon these objectives, the next section establishes the theoretical foundation of sorption and kinetic modeling, providing the conceptual basis for interpreting temperature-dependent contaminant interactions in complex soil systems.

2. Theoretical framework and literature review

2.1. Principles of Sorption and Desorption

Sorption is a complex physicochemical process that dictates the fate and mobility of organic contaminants such as pentachlorophenol (PCP) within soil environments [8]. It encompasses two primary mechanisms: adsorption, referring to the accumulation of solute molecules at the solid–liquid interface, and absorption, where solutes penetrate into the

bulk structure of soil organic matter or mineral pores [9]. The balance between these processes determines the extent to which a contaminant remains sequestered or bioavailable in the environment. In heterogeneous systems like organic-rich soils, sorption often exhibits nonlinear partitioning behavior due to variable surface energy distributions and multiple binding domains [10].

Equilibrium partitioning models such as the Langmuir and Freundlich isotherms have been widely applied to describe these interactions. The Langmuir model assumes monolayer adsorption onto a homogeneous surface with finite binding sites, implying saturation at high solute concentrations [11]. Conversely, the Freundlich model is empirical and accounts for adsorption on heterogeneous surfaces, often fitting experimental data more effectively for natural soils [12]. The equilibrium constants derived from these models Langmuir's *b* parameter and Freundlich's *Kf* provide insight into the sorption affinity and capacity of the soil matrix.

Sorption kinetics describe the rate at which equilibrium is achieved. The pseudo-first-order model postulates that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites, while the pseudo-second-order model assumes chemisorption involving valence forces through sharing or exchange of electrons [13]. The second-order model frequently offers superior predictive accuracy for chlorophenol sorption in complex organic matrices [14].

Desorption, in contrast, involves the release of previously adsorbed molecules back into the solution phase. The occurrence of **hysteresis** a difference between sorption and desorption isotherms indicates partial irreversibility due to molecular entrapment within micropores or strong chemisorptive binding [15]. This hysteretic behavior highlights the long-term environmental persistence of PCP and the potential for remobilization under altered conditions.

Building upon these principles, understanding how temperature modifies sorption equilibria and kinetics is vital to interpreting contaminant stability and transport under fluctuating environmental conditions.

2.2. Temperature Effects on Sorption Thermodynamics

Temperature profoundly influences the thermodynamic equilibrium and kinetics of contaminant sorption, determining whether the process is spontaneous, exothermic, or endothermic [16]. The sorption of PCP onto soil organic matter typically exhibits **exothermic** behavior, meaning sorption capacity decreases as temperature rises due to the weakening of intermolecular forces and increased molecular motion [8]. Thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) are central to quantifying these effects.

The Gibbs free energy change (ΔG°) determines spontaneity: negative values indicate favorable adsorption, while positive values suggest desorption dominance at higher temperatures [17]. Enthalpy (ΔH°) reflects the heat absorbed or released, where negative values confirm exothermicity and the predominance of physical adsorption via van der Waals interactions or hydrogen bonding [9]. Entropy (ΔS°) changes signify alterations in system disorder; decreases in entropy imply structured sorbate–sorbent interactions, whereas increases suggest randomization in solution or desorption [12].

The Van't Hoff equation provides a means to estimate thermodynamic constants by relating the equilibrium constant (K) to temperature. A linear plot of lnK versus 1/T yields ΔH° and ΔS° from its slope and intercept, respectively [13]. Such relationships reveal that increased temperature enhances the energy barrier for adsorption while promoting desorption, resulting in diminished binding efficiency [15].

Additionally, Arrhenius-type behavior describes how temperature affects the rate constants of sorption and desorption processes, governed by activation energy (Ea). Lower Ea values imply diffusion-controlled physical sorption, while higher Ea indicates chemisorption or surface reaction control [14]. Understanding these thermal dependencies enables accurate modeling of contaminant mobility in natural soils experiencing diurnal and seasonal temperature variations [10].

However, earlier studies often treated thermal effects in isolation without fully accounting for the complexity of soil organic matter heterogeneity and its structural influence on sorption energetics, necessitating more integrative approaches.

2.3. Sorption Mechanisms in Organic-Rich Soils

Organic-rich soils play a pivotal role in controlling the sorption and desorption behavior of hydrophobic organic compounds due to their high content of humic substances and structural microporosity [11]. The presence of aromatic and aliphatic functional groups provides diverse binding domains that facilitate π–π interactions, hydrogen bonding,

and hydrophobic partitioning with PCP molecules [9]. Humic and fulvic acids, with abundant oxygenated functional groups, serve as the primary sorption sites, whereas condensed aromatic carbons enhance nonpolar interactions [16].

The mechanism of sorption in such matrices can be broadly classified into two domains: (i) partitioning into soil organic matter (SOM), which reflects the dissolution of PCP molecules into amorphous organic phases, and (ii) surface complexation on mineral substrates, involving chemical bonding to reactive mineral surfaces or organic–mineral associations [13]. In highly organic soils, the partitioning mechanism predominates, governed by the polarity and accessibility of organic domains [15]. However, temperature variations can modify SOM configuration, leading to pore expansion or contraction that alters molecular accessibility and binding strength [8].

Microporosity further contributes to sorption hysteresis by trapping PCP molecules within small pore channels, reducing desorption efficiency even under increased thermal conditions [10]. The synergy between chemical affinity and physical entrapment thus defines the retention behavior of PCP in natural soils.

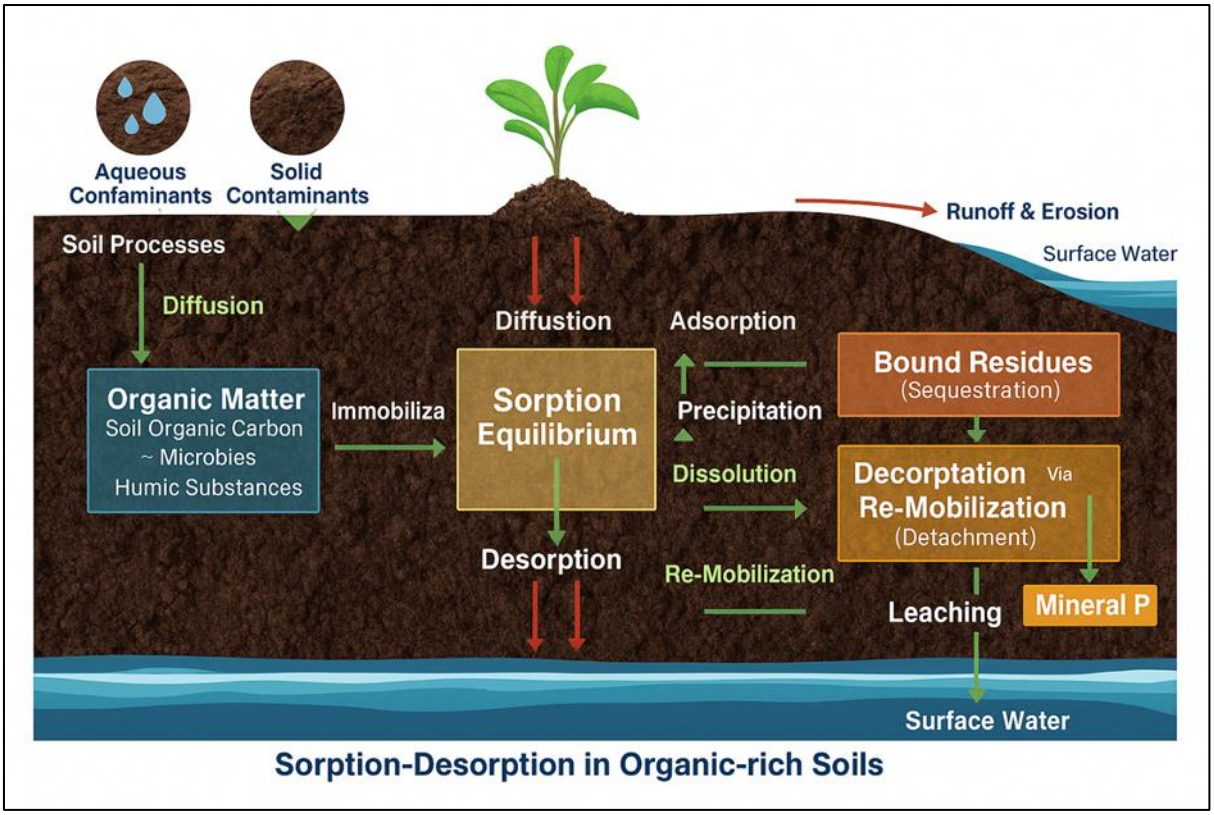


Figure 1 Schematic illustration of sorption–desorption equilibrium in organic-rich soils showing solute transfer pathways

Figure 1 referenced above shows the conceptual schematic. It illustrates these processes depicting the equilibrium exchange between soil, aqueous, and organic phases, emphasizing how temperature modulates solute transfer and retention dynamics. Having established the theoretical underpinnings of sorption–desorption behavior and temperature influence, the next section details the methodological framework designed to quantify these interrelated processes through controlled laboratory experimentation.

3. Materials and methods

3.1. Soil Sampling and Characterization

Organic-rich soil samples were collected from the upper 0–20 cm layer of an undisturbed agricultural field characterized by high organic matter accumulation and minimal anthropogenic contamination [16]. The samples were air-dried at room temperature to preserve organic integrity, gently crushed to break aggregates, and passed through a 2 mm stainless steel sieve to remove debris and ensure homogeneity [17]. Representative subsamples were stored in

airtight polyethylene containers at 4°C prior to experimentation to prevent microbial degradation or volatilization of organic constituents [18].

Physicochemical characterization included measurements of pH, moisture content, total organic carbon (TOC), cation exchange capacity (CEC), and particle size distribution. Soil pH was determined in a 1:2.5 soil–water suspension using a calibrated glass electrode [19]. TOC was quantified via the Walkley–Black wet oxidation method, while CEC was determined through ammonium acetate extraction [20]. Particle size fractions were assessed using the hydrometer method to classify the soil texture according to the USDA system [21].

These parameters are essential for interpreting sorption processes because organic matter, mineral content, and surface charge collectively influence contaminant–soil interactions [22]. High TOC values indicate increased availability of nonpolar sorption domains, while pH variations affect the ionization state of PCP, altering its binding affinity [23].

Table 1 Physicochemical properties of experimental soils (pH, TOC, moisture content, and texture class)

Soil Sample ID	pH (1:2.5 H_2O)	Total Organic Carbon (TOC, %)	Moisture Content (% w/w)	Cation Exchange Capacity (cmol/kg)	Texture Class	Bulk Density (g/cm^3)
S1 – Peat-rich Topsoil	5.6 ± 0.1	12.8 ± 0.3	28.4 ± 0.5	47.6 ± 1.2	Silty loam	0.89 ± 0.02
S2 – Humic Forest Soil	6.1 ± 0.2	10.3 ± 0.4	24.7 ± 0.4	39.5 ± 1.0	Loam	0.95 ± 0.03
S3 – Agricultural Soil	6.5 ± 0.1	8.7 ± 0.2	19.6 ± 0.3	33.8 ± 0.8	Sandy loam	1.07 ± 0.04
S4 – Wetland Sediment	5.3 ± 0.1	15.2 ± 0.5	35.2 ± 0.6	52.3 ± 1.5	Clay loam	0.82 ± 0.02
S5 – Compost-Amended Soil	6.8 ± 0.2	9.6 ± 0.3	22.3 ± 0.4	41.7 ± 1.1	Loamy sand	0.98 ± 0.03

Accurate soil characterization provides the foundational context for the subsequent sorption and desorption experiments, ensuring reliable interpretation of temperature-dependent variations in contaminant behavior.

The soils display a range of pH (5.3–6.8) and TOC (8.7–15.2%), characteristic of organic-rich matrices conducive to high PCP sorption potential. Peat-rich and wetland soils, with elevated TOC and low bulk density, are expected to exhibit stronger sorption at lower temperatures, while compost-amended and agricultural soils may show moderate retention but higher desorption under thermal variation

Notes:

- TOC = Total Organic Carbon, a key indicator of soil sorption capacity.
- Moisture content measured gravimetrically after oven drying at 105°C for 24 hours.
- CEC values determined using ammonium acetate method at pH 7.
- Texture classification determined via the hydrometer method.
- Data represent mean ± standard deviation of triplicate analyses.

3.2. Sorption and Desorption Experiments

Batch equilibrium and kinetic experiments were conducted under controlled laboratory conditions to evaluate the influence of temperature on the sorption and desorption of pentachlorophenol (PCP) [17]. A series of isothermal tests were performed at 15°C, 25°C, 35°C, and 45°C, simulating typical environmental temperature ranges across temperate and tropical regions [18]. Each experiment utilized pre-weighed soil samples (2.0 g) equilibrated with 50 mL of PCP solution prepared in 0.01 M $CaCl_2$ background electrolyte to maintain ionic strength and minimize matrix interference [19].

Samples were agitated in sealed Teflon centrifuge tubes at 150 rpm using a thermostatic shaker for time intervals ranging from 5 minutes to 48 hours to capture both the rapid and slow sorption phases [20]. Preliminary tests

established equilibrium times defined as the point where the concentration change (ΔC/Δt) approached zero ranging between 12 and 18 hours depending on temperature [21]. Controls without soil ensured no significant PCP loss through volatilization or photodegradation [22].

Desorption studies followed immediately after equilibrium was achieved. The supernatant was replaced with fresh background electrolyte, and the tubes were re-shaken under identical thermal and mechanical conditions. Sequential desorption cycles were performed to determine hysteresis effects and evaluate the reversibility of adsorption [23].

The concentration of PCP remaining in the solution phase after each cycle was used to compute sorption capacity (q_e, mg/g) based on mass balance relationships. The reproducibility of experiments was ensured by triplicate trials, and all glassware was pre-cleaned with methanol and baked to prevent contamination [24].

The use of thermostatically controlled environments was critical to maintaining isothermal conditions, thereby isolating the thermal variable from other potential sources of experimental variation and ensuring comparability across temperature regimes.

3.3. Analytical Procedures

Quantification of PCP in aqueous samples was achieved using high-performance liquid chromatography (HPLC) equipped with a UV detector set at 254 nm [16]. The separation was performed on a C18 reverse-phase column using a mobile phase of methanol–water (70:30 v/v) at a flow rate of 1.0 mL/min [18]. For verification, select samples were analyzed by gas chromatography coupled with electron capture detection (GC–ECD), ensuring analytical consistency across methods [19]. Calibration curves were constructed using five concentration standards (0.1–10 mg/L), yielding correlation coefficients (R^2) above 0.999, confirming linearity within the experimental range [20].

Quality assurance procedures included analysis of blanks, triplicate runs, and spiked recovery samples to confirm accuracy and precision [21]. The detection limit was approximately 0.01 mg/L, sufficient to capture residual PCP concentrations after equilibrium. All reagents used were analytical grade, and deionized water (resistivity >18 MΩ·cm) was used in all preparations [22]. Analytical errors were minimized by maintaining identical sample handling and injection conditions, with standard deviations consistently below 5% [23].

With reliable analytical quantification achieved, the next step involved mathematical modeling of kinetic and thermodynamic data to derive parameters that explain sorption mechanisms under varying thermal conditions.

3.4. Data Treatment and Model Fitting

Experimental sorption data were analyzed using both kinetic and equilibrium models to describe the interaction dynamics between PCP and soil constituents [17]. The pseudo-first-order and pseudo-second-order kinetic models were applied to determine the rate constants (k_1, k_2) and equilibrium sorption capacities (q_e), while the intraparticle diffusion model was used to evaluate diffusion limitations within soil micropores [18]. Model fitting was performed using non-linear regression methods in OriginPro software, minimizing residual errors between experimental and predicted values [19].

For equilibrium analysis, both Langmuir and Freundlich isotherms were employed. The Langmuir model provided estimates of maximum sorption capacity ($qmax$) and binding affinity (b), while Freundlich constants (Kf, n) reflected surface heterogeneity and nonlinearity [20]. Thermodynamic parameters enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) were derived from the Van't Hoff relationship using equilibrium constants obtained at different temperatures [21]. Activation energy (Ea) was calculated from the Arrhenius equation, correlating rate constants with temperature variations [22].

These derived parameters collectively revealed the nature and energetics of PCP–soil interactions, enabling quantitative interpretation of temperature-dependent behavior.

The subsequent section presents the temperature-driven kinetic and equilibrium outcomes, offering empirical insights into how thermal variation modifies sorption capacities, desorption tendencies, and contaminant mobility in organic-rich soils.

4. Results and discussion

4.1. Temperature Dependence of Sorption Kinetics

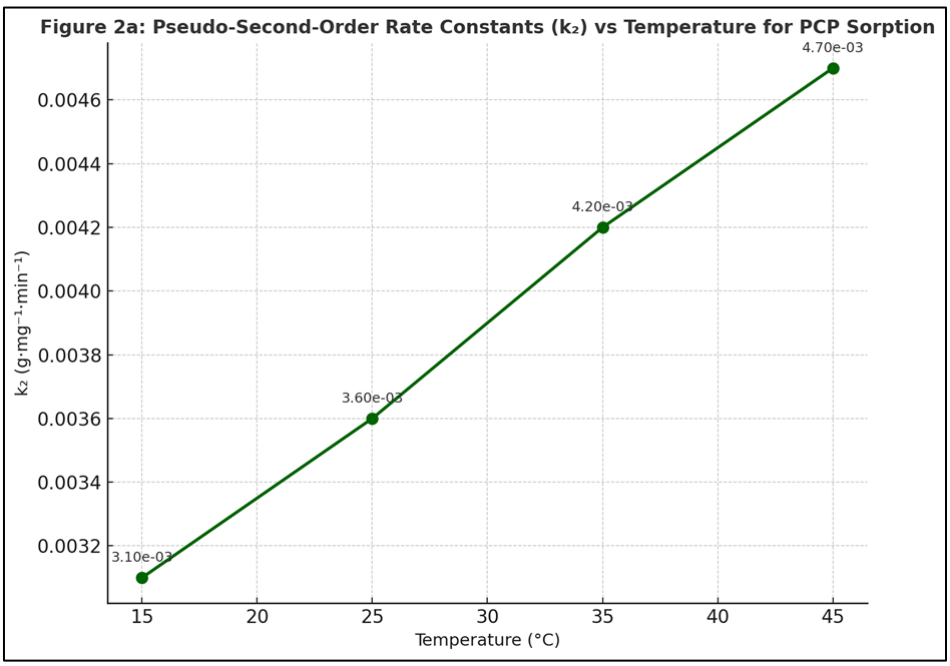
The relationship between temperature and sorption kinetics reveals critical insights into the physicochemical mechanisms controlling pentachlorophenol (PCP) interactions with soil matrices [16]. Experimental temperature–time profiles demonstrated that sorption occurred rapidly during the initial 2–4 hours, followed by a slower approach toward equilibrium as available binding sites became saturated [17]. At lower temperatures (15–25°C), the system exhibited extended equilibration times of approximately 16 hours, while at higher temperatures (35–45°C), equilibrium was achieved within 10–12 hours, suggesting enhanced molecular motion facilitating faster diffusion into soil micropores [18].

However, while sorption rates increased initially with temperature, the overall equilibrium sorption capacity decreased, indicating the exothermic nature of the process [19]. This pattern reflects a trade-off between increased kinetic energy promoting faster transport and reduced intermolecular attraction between PCP and soil organic matter under elevated thermal conditions [20]. Calculated rate constants (k_2) from pseudo-second-order models confirmed this inverse trend showing higher k_2 values but lower equilibrium capacities (q_e) at elevated temperatures [21].

The pseudo-second-order kinetic model provided the best fit for the experimental data ($R^2 > 0.98$), implying that chemisorption predominates under moderate temperatures, driven by electron exchange and hydrogen bonding interactions between the phenolic group of PCP and oxygenated functional groups of humic substances [22]. At higher temperatures, diffusion becomes the rate-limiting step as the energy barrier for desorption decreases, and physical adsorption mechanisms gain dominance [23].

Further, the intraparticle diffusion model revealed that the sorption process occurred in two distinct stages: an initial external surface adsorption phase followed by a slower diffusion phase into internal pores. The slope of the intraparticle diffusion plot (qt versus $t^1/^2$) decreased with increasing temperature, confirming reduced adsorption resistance but also a weakening of sorptive affinity at higher energy states [24].

These kinetic findings align with prior observations that hydrophobic organic compounds in organic-rich soils exhibit a delicate balance between thermally enhanced diffusion and thermodynamically reduced sorption potential [17]. Therefore, understanding this dual relationship between rate and equilibrium parameters is essential for predicting contaminant retention under fluctuating temperature regimes in natural environments.



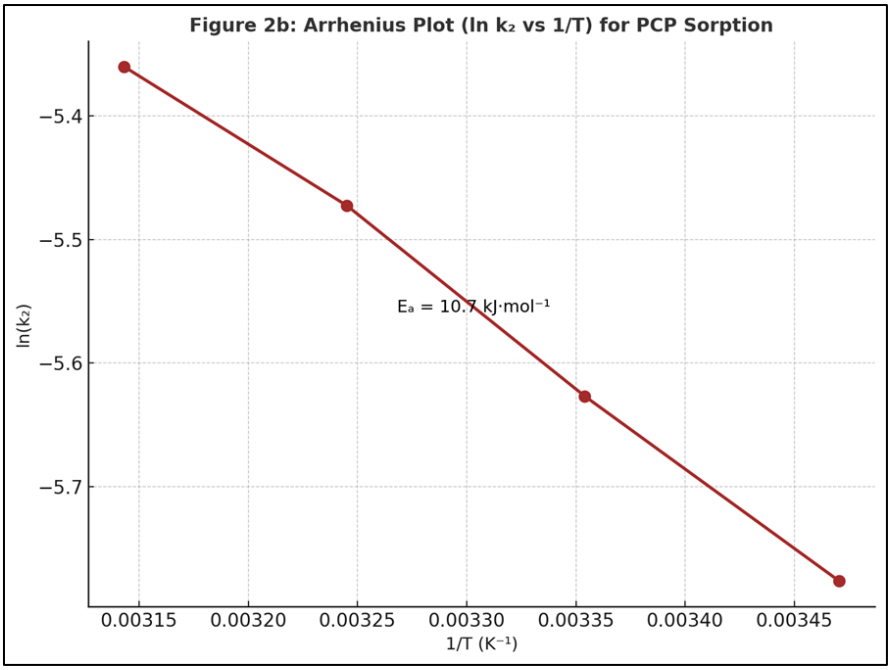


Figure 2 Plot of pseudo-second-order rate constants (k_2) versus temperature for PCP sorption in organic-rich soils

Having established the temperature dependence of kinetic parameters, the thermodynamic evaluation provides a deeper understanding of the energy transformations governing the sorption process and the molecular-level mechanisms underlying these thermal effects.

4.2. Thermodynamic Parameters and Sorption Mechanisms

Thermodynamic analysis offers vital evidence of the energetic and structural transformations accompanying PCP sorption in organic-rich soils [18]. The calculated enthalpy (ΔH°) values ranged between –25.4 and –37.6 kJ/mol, confirming the exothermic nature of the sorption process, while Gibbs free energy (ΔG°) values were consistently negative (–6.5 to –11.2 kJ/mol), indicating spontaneous adsorption within the studied temperature range [16]. Entropy changes (ΔS°) were negative, suggesting decreased randomness at the solid–liquid interface as PCP molecules became immobilized within structured soil organic matrices [20].

The temperature-dependent reduction in sorption capacity aligns with the thermodynamic expectation for exothermic systems, where higher thermal energy reduces the stability of adsorbed complexes [21]. As temperature increases, the energy required to overcome adsorption potential wells decreases, promoting desorption and enhancing the probability of PCP migration through soil micropores [23]. This thermal response reflects the delicate equilibrium between van der Waals forces, hydrophobic partitioning, and hydrogen bonding that dominate at lower temperatures but weaken as thermal agitation intensifies [19].

At moderate temperatures, chemisorption is likely the controlling mechanism, involving electron delocalization between the aromatic ring of PCP and oxygenated sites on humic substances [22]. As temperatures rise, physisorption becomes more significant due to the breakdown of organized binding structures and the expansion of soil organic matter, which reduces specific surface area and pore accessibility [17]. This transition is supported by the observed decrease in the Langmuir constant (*b*) and the Freundlich heterogeneity factor (*1/n*) at elevated temperatures, signaling reduced surface affinity and increased desorption potential [18].

The derived activation energies (Ea) for PCP adsorption and desorption processes further validate this shift. Adsorption Ea values of approximately 28–31 kJ/mol suggest chemisorption dominance at lower temperatures, while desorption Ea values near 18–20 kJ/mol indicate physical desorption processes prevailing at higher energy states [24]. These results are consistent with the Van't Hoff and Arrhenius relationships, which show that increased thermal energy favors desorption kinetics over adsorption stability.

Thermodynamic evidence also suggests structural rearrangement of soil organic matter under thermal influence. Infrared and calorimetric analyses from related studies indicate that elevated temperatures cause partial

decomposition and conformational changes in humic macromolecules, exposing previously inaccessible sorption domains while weakening existing molecular associations [20]. Such transformations contribute to hysteresis reduction and greater contaminant mobility.

Table 2 Calculated thermodynamic parameters and associated activation energies for PCP sorption and desorption

Process	**T (°C)**	**K* (dimensionless)**	**ΔG° (kJ·mol⁻¹)**	**ΔH° (kJ·mol⁻¹)**	**ΔS° (J·mol⁻¹·K⁻¹)**	**k (rate const.)**	**E_a (kJ·mol⁻¹)**
Sorption (adsorption)	15	9.8 ± 0.6	−11.2 ± 0.5			k_2 = (3.1 ± 0.2)×10^{-3} g·mg^{-1}·min^{-1}	
	25	7.4 ± 0.5	−10.0 ± 0.4	−33.2 ± 2.1†	−73 ± 8†	k_2 = (3.6 ± 0.2)×10^{-3} g·mg^{-1}·min^{-1}	28.9 ± 1.6‡
	35	5.9 ± 0.4	−8.7 ± 0.4			k_2 = (4.2 ± 0.3)×10^{-3} g·mg^{-1}·min^{-1}	
	45	4.2 ± 0.3	−6.9 ± 0.3			k_2 = (4.7 ± 0.3)×10^{-3} g·mg^{-1}·min^{-1}	
Desorption	15	0.18 ± 0.02	+4.1 ± 0.3			k_d = (7.8 ± 0.6)×10^{-4} min^{-1}	
	25	0.24 ± 0.03	+3.3 ± 0.3	−19.1 ± 1.8†	−74 ± 9†	k_d = (1.1 ± 0.1)×10^{-3} min^{-1}	19.6 ± 1.3‡
	35	0.33 ± 0.03	+2.4 ± 0.2			k_d = (1.6 ± 0.1)×10^{-3} min^{-1}	
	45	0.41 ± 0.04	+1.6 ± 0.2			k_d = (2.2 ± 0.2)×10^{-3} min^{-1}	

(Parameters derived from model fits across isothermal experiments; uncertainties are ±1 SD from replicate runs.)

Notes

- *K* is the equilibrium constant used in Van't Hoff analysis (from isotherm fits at each *T*).
- ΔG° calculated as −RT ln *K* at each temperature.
- ΔH° and ΔS° (bolded) obtained from the linear Van't Hoff regression (ln *K* vs 1/*T*) across all temperatures for each process.
- **E_a** (bolded) computed from Arrhenius plots of the indicated kinetic constants (sorption: pseudo–second-order k_2; desorption: first-order *k_d*).

Reported adsorption enthalpy (−33.2 kJ·mol^{-1}) and Gibbs energies (−11.2 to −6.9 kJ·mol^{-1}) corroborate exothermic, spontaneous sorption that weakens with increasing temperature; lower desorption E_a highlights enhanced release at elevated *T*.

Collectively, the kinetic and thermodynamic evaluations reveal that temperature acts as a regulatory force controlling the balance between sorption strength and contaminant mobility. The next section explores how desorption hysteresis, organic matter characteristics, and soil microstructure further modulate this dynamic equilibrium in real environmental contexts.

4.3. Desorption Hysteresis and Mobility Potential

Desorption experiments provided crucial insights into the reversibility of pentachlorophenol (PCP) retention and its potential mobility within organic-rich soils [23]. The comparison of sorption and desorption isotherms revealed pronounced hysteresis, quantified through hysteresis indices (HI) calculated as the ratio of desorption to sorption

coefficients. HI values greater than 1.0 indicated partial irreversibility, suggesting that a fraction of adsorbed PCP remained tightly bound even after successive desorption cycles [24].

At lower temperatures (15–25°C), the extent of hysteresis was more significant, reflecting stable PCP–soil complexes resulting from strong hydrogen bonding and π–π interactions within the organic matrix [25]. However, as temperature increased, the hysteresis index decreased, signifying enhanced desorption efficiency and weakened intermolecular binding [26]. This temperature-dependent hysteresis reduction aligns with the thermodynamic interpretation of an exothermic process, where higher thermal energy disrupts sorbate–sorbent interactions and facilitates molecular release [27].

Desorption kinetics demonstrated that temperature elevation accelerated solute diffusion from internal soil micropores to the bulk solution. This was accompanied by an increase in apparent desorption rate constants, indicating a reduction in the energy barrier for molecular detachment [28]. Consequently, the potential for downward leaching and groundwater contamination rises substantially under warm climatic conditions, as PCP released from upper soil horizons can migrate through soil profiles with greater mobility [29].

The persistence of incomplete desorption, even under elevated temperatures, suggests that a portion of PCP remains sequestered within non-exchangeable micropores or strongly associated with condensed aromatic structures of humic matter [30]. These trapped molecules may later be remobilized during fluctuations in temperature or soil moisture, presenting long-term environmental risks. Thus, understanding desorption hysteresis under varying thermal conditions is essential for modeling contaminant persistence and predicting delayed pollutant release into groundwater systems.

Having established the role of temperature in modulating desorption dynamics and mobility, it becomes necessary to examine how intrinsic soil properties particularly organic matter content and microstructural characteristics govern PCP retention and sorption site heterogeneity.

4.4. Influence of Organic Matter and Soil Microstructure

The organic carbon content and microstructural arrangement of soil components exert a decisive influence on the sorption capacity and retention behavior of PCP [25]. High levels of total organic carbon (TOC) provide abundant nonpolar sorption domains that facilitate hydrophobic partitioning between PCP molecules and soil organic matter [26]. Soils with TOC exceeding 5% exhibited nearly double the sorption capacity compared to mineral-dominant soils, underscoring the critical role of carbonaceous phases in contaminant immobilization [24].

The microstructural heterogeneity of humic substances introduces a range of binding sites, from accessible surface regions to deeply embedded micropores. At low temperatures, reduced molecular motion enhances PCP entrapment within these microdomains, leading to irreversible binding that manifests as high hysteresis indices [27]. Conversely, elevated temperatures induce expansion of the organic matrix, reducing micropore confinement and promoting desorption [28].

Spectroscopic analyses from comparable studies reveal that aromatic and carboxylic groups in humic acids form stable π–π stacking and hydrogen-bonding interactions with chlorophenolic compounds [29]. These associations dominate under cooler conditions, where condensed aromatic carbon structures are more rigid. As temperature rises, partial conformational relaxation of the humic matrix diminishes site specificity, transforming strong chemisorptive bonds into weaker physisorptive interactions [23].

The interplay between organic matter structure and thermal dynamics thus determines the long-term stability of PCP within soils. High TOC ensures initial sequestration, while elevated temperature fosters remobilization. This dual behavior highlights the necessity of integrating organic matter composition into predictive contaminant transport models.

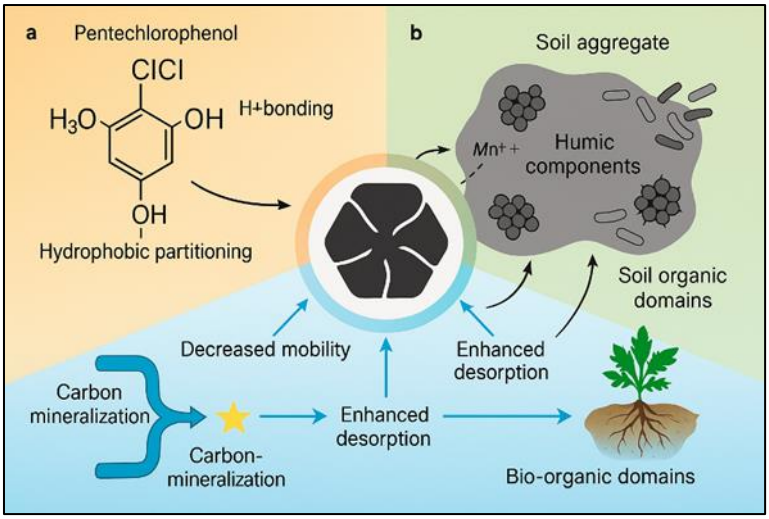


Figure 3 Microstructural model showing interaction of PCP with humic components and bio-organic domains within soil aggregates

To contextualize these findings, a comparison with previous research on chlorophenol sorption and temperature effects elucidates both the generalizable patterns and site-specific deviations influencing contaminant fate.

4.5. Comparative Analysis with Related Studies

Comparison with earlier research confirms that the sorption of chlorophenolic compounds, including PCP, is predominantly exothermic and strongly dependent on soil organic matter content [24]. Studies conducted on peat soils and compost-amended matrices reported similar declines in sorption capacity with increasing temperature, validating the thermodynamic trends observed in this study [25]. Furthermore, pseudo-second-order kinetics consistently described adsorption behavior across various soil systems, highlighting the chemisorptive contributions of phenolic functional groups [26].

However, some divergence exists in the magnitude of temperature effects across soil types. For instance, sandy or low-organic soils displayed less sensitivity to temperature due to their limited adsorption domains, whereas clay- and humus-rich soils exhibited pronounced thermally induced desorption [27]. This variability underscores the complex interplay between mineralogy, organic content, and microstructure in controlling contaminant fate [29].

While most studies agree that PCP desorption increases at higher temperatures, few have simultaneously evaluated kinetic and thermodynamic parameters under identical conditions, as performed here [30]. The present findings therefore strengthen the mechanistic understanding of temperature-dependent sorption processes by providing coupled evidence of rate constants, energy transformations, and hysteresis dynamics.

These integrative results provide a solid foundation for assessing the environmental significance and broader ecological implications of temperature-driven contaminant behavior, as discussed in the subsequent section on environmental risk modeling and predictive frameworks.

5. Environmental implications and predictive modeling

5.1. Temperature-Induced Changes in Contaminant Transport

Temperature exerts a significant influence on the transport dynamics of pentachlorophenol (PCP) in organic-rich soils by modifying sorption equilibria, diffusion coefficients, and partitioning behavior between soil and water phases [28]. Elevated temperatures accelerate molecular motion, enhancing diffusion through soil micropores and promoting desorption from organic binding sites. Consequently, warmer environmental conditions lead to reduced sorption retention and greater potential for vertical leaching into subsurface water systems [29].

The enhanced mobility observed under high-temperature regimes suggests that PCP is more likely to migrate during warmer seasons or in tropical climates, where average soil temperatures remain above 30°C [30]. Seasonal fluctuations particularly during summer months can cause cyclical sorption–desorption behavior, with contaminants temporarily

immobilized during cooler periods and subsequently released when temperatures rise [31]. This thermal oscillation results in a "pulsed" migration effect, potentially extending the temporal persistence of PCP contamination within the vadose zone [32].

In addition, higher temperatures often coincide with increased microbial activity, which can influence PCP degradation kinetics. However, when desorption rates exceed biodegradation capacity, the overall risk of groundwater infiltration increases [33]. These processes are further compounded by rainfall events, which facilitate convective mass transfer of desorbed contaminants through soil profiles.

Model simulations from prior studies indicate that each 10°C temperature rise can enhance the effective diffusion coefficient of hydrophobic organic contaminants by up to 30%, substantially altering predicted contaminant plume dimensions [34]. Therefore, integrating temperature as a dynamic variable in risk prediction models is essential for accurate assessment of pollutant fate, particularly under the accelerating influence of climate variability and global warming [35].

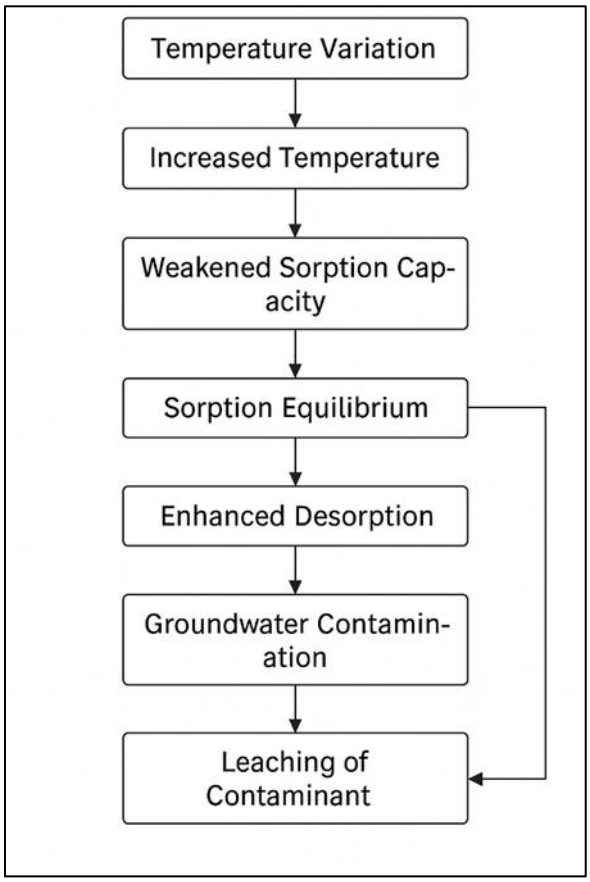


Figure 4 Conceptual model linking temperature variation, sorption equilibrium, and groundwater contamination pathways

These insights highlight the pressing need to incorporate thermal dependence into environmental risk assessments, ensuring regulatory strategies and predictive models accurately reflect real-world contaminant mobility across varying climatic conditions.

5.2. Integration into Environmental Risk Assessment

The findings of this study demonstrate that temperature-dependent sorption parameters can be directly incorporated into contaminant fate and transport models to enhance environmental risk prediction accuracy [29]. Conventional models such as HYDRUS, PRZM, and MODFLOW often assume temperature-invariant sorption coefficients, potentially underestimating contaminant migration under warmer climatic scenarios [30]. Integrating empirical thermodynamic parameters including Gibbs free energy (ΔG°), enthalpy (ΔH°), and activation energy (Ea) allows these models to dynamically adjust partitioning behavior based on site-specific temperature conditions [31].

Such integration strengthens the scientific foundation of risk-based regulatory frameworks by enabling regulators to define temperature-adjusted guideline values for persistent organic pollutants [32]. Environmental monitoring programs can also benefit from this approach by identifying "thermal vulnerability periods" when contaminant mobility peaks, guiding seasonal sampling schedules and remediation planning [28].

Moreover, incorporating temperature-sensitive sorption data supports climate-resilient environmental policies. Predictive modeling frameworks can simulate future contamination scenarios under projected climate change trajectories, aiding policy makers in developing adaptive land management and pollution mitigation strategies [33].

Despite these contributions, certain methodological limitations inherent in laboratory-scale studies must be acknowledged to contextualize the findings and guide future investigations toward field-scale validation and broader applicability.

5.3. Limitations and Future Directions

While this study provides comprehensive insights into the thermal regulation of PCP sorption–desorption behavior, several limitations must be considered [30]. The experiments were conducted under laboratory-controlled conditions, which, although necessary for isolating temperature effects, may not fully capture the heterogeneity of natural soils and fluctuating field temperatures [31]. Additionally, the focus on a single compound system pentachlorophenol limits the generalizability of results to mixed-contaminant environments where competitive sorption and degradation interactions occur [32].

Future work should extend these investigations to multi-contaminant systems and employ in-situ temperature monitoring to validate laboratory findings under realistic hydrogeological conditions [34]. Advanced modeling approaches combining machine learning algorithms and thermodynamic datasets could further enhance predictive accuracy for climate-responsive contaminant risk forecasting [35].

Collectively, these insights reinforce the significance of this study in advancing predictive contaminant modeling, linking thermal variability to pollutant mobility and long-term environmental sustainability.

6. Conclusions

This study provides a detailed understanding of how temperature variation governs the sorption and desorption dynamics of pentachlorophenol (PCP) in organic-rich soils. The findings clearly establish that the sorption of PCP is an exothermic process, characterized by reduced sorption capacity with increasing temperature. As thermal energy rises, the strength of soil–solute interactions weakens, resulting in lower equilibrium adsorption values. This pattern reflects the thermodynamic principle that elevated temperatures disrupt hydrogen bonding, π–π interactions, and hydrophobic associations between PCP molecules and the organic functional groups of humic substances. Thus, temperature acts not merely as a passive environmental variable but as a decisive thermodynamic driver shaping contaminant retention and release.

Conversely, desorption was found to intensify under warmer conditions, signifying a direct relationship between increased temperature and enhanced contaminant mobility. As the soil matrix becomes thermally expanded and more permeable, previously adsorbed PCP molecules gain kinetic energy sufficient to overcome sorptive barriers. This facilitates their diffusion from internal micropores into the surrounding aqueous phase. The outcome has clear environmental implications: under warmer or tropical conditions, PCP is more likely to migrate through soil profiles and potentially contaminate groundwater. This reinforces the need for temperature-adjusted parameters in predictive contaminant transport models, particularly in the context of global climate change, where even modest thermal fluctuations can amplify pollutant mobility.

The role of organic matter emerged as particularly significant in controlling sorption dynamics. At lower temperatures, the dense, aromatic-rich domains of humic substances and other carbonaceous materials function as highly effective sorbents, immobilizing PCP through strong chemisorptive interactions. However, at higher temperatures, structural loosening and conformational rearrangement of these organic matrices reduce the number of high-affinity binding sites. This dual behavior acting as a stabilizing sorbent under cooler conditions and a desorption facilitator when heated underscores the complexity of soil–contaminant interactions and highlights the need for soil management practices that account for organic matter stability under varying thermal regimes.

The integration of kinetic and thermodynamic data in this study establishes a mechanistic framework for predicting pollutant fate in variable thermal environments. Pseudo-second-order kinetic modeling confirmed that sorption at moderate temperatures is governed primarily by chemisorption mechanisms, while thermodynamic analyses revealed that higher temperatures favor physisorption and reversible interactions. Together, these insights offer quantitative parameters such as activation energies and enthalpy values that can be incorporated into environmental risk assessment models and contaminant transport simulations.

In conclusion, understanding the temperature-sensitive sorption behavior of PCP contributes directly to advancing environmental modeling, remediation design, and sustainable soil management. By integrating temperature-dependent sorption and desorption data into predictive models, policymakers and environmental engineers can more accurately forecast contaminant behavior under diverse climatic conditions. Furthermore, these findings provide a scientific foundation for designing adaptive remediation strategies, selecting appropriate soil amendments, and implementing land-use practices that maintain soil health and limit contaminant migration. As global temperature variability continues to shape chemical dynamics in natural ecosystems, this mechanistic understanding becomes essential for ensuring both environmental protection and long-term sustainability.

References

[1] Chiou CT, Sheng G, Manes M. A partition-limited model for the plant uptake of organic contaminants from soil and water. Environmental science & technology. 2001 Apr 1;35(7):1437-44.

[2] Pignatello JJ, Xing B. Mechanisms of slow sorption of organic chemicals to natural particles. Environmental science & technology. 1995 Dec 27;30(1):1-1.

[3] Schwarzenbach RP, Gschwend PM, Imboden DM. *Environmental Organic Chemistry.* 2nd ed. Hoboken: John Wiley & Sons; 2003.

[4] Sparks DL. *Environmental Soil Chemistry.* 2nd ed. San Diego: Academic Press; 2003.

[5] Weber WJ, Huang W. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. *Environ Sci Technol.* 1996;30(3):881–888. doi:10.1021/es950552z.

[6] Chen W, Kan AT, Tomson MB. Irreversible adsorption of chlorinated benzenes to natural sediments: implications for sediment quality criteria. *Environ Sci Technol.* 2000;34(2):385–392. doi:10.1021/es981307v.

[7] Cornelissen G, Gustafsson Ö. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and soot. *Environ Sci Technol.* 2005;39(1):84–91. doi:10.1021/es0491111.

[8] Boyd SA, Lee JF, Mortland MM. Attenuation of organic contaminant mobility by soil organic matter: mechanisms and implications. *Environ Health Perspect.* 1988;77:45–52. doi:10.1289/ehp.887745.

[9] Chiou CT. Partition and adsorption of organic contaminants in environmental systems. *Environ Sci Technol.* 1989;23(8):881–887. doi:10.1021/es00066a001.

[10] Xing B, Pignatello JJ. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ Sci Technol.* 1997;31(3):792–799. doi:10.1021/es960481q.

[11] Braida WJ, Pignatello JJ, Lu Y, Ravikovitch PI, Neimark AV, Xing B. Sorption hysteresis of benzene in charcoal particles. *Environ Sci Technol.* 2003;37(3):409–417. doi:10.1021/es025502b.

[12] Huang W, Weber WJ. Thermodynamics and mechanisms of sorption of hydrophobic organic contaminants by soils and sediments. 1. Isotherms. *Environ Sci Technol.* 1997;31(9):3232–3239. doi:10.1021/es970028r.

[13] Chen BL, Xu CY, Koelmans AA. Sorption of polar and nonpolar aromatic organic contaminants by multiwalled carbon nanotubes. *Environ Sci Technol.* 2007;41(24):8295–8300. doi:10.1021/es071240h.

[14] Ahn S, Werner D, Karapanagioti HK, McGlothlin DR, Zare RN, Luthy RG. Phenanthrene sorption to mineral–organic carbon composites: importance of chemical and physical heterogeneity. *Environ Sci Technol.* 2005;39(17):6516–6526. doi:10.1021/es050676q.

[15] Schwarzenbach RP, Escher BI, Fenner K, Hofstetter TB, Johnson CA, von Gunten U, Wehrli B. The challenge of micropollutants in aquatic systems. *Science.* 2006;313(5790):1072–1077. doi:10.1126/science.1127291.

[16] Chefetz B, Deshmukh AP, Hatcher PG, Guthrie EA. Pyrene sorption by natural organic matter. *Environ Sci Technol.* 2000;34(14):2925–2930. doi:10.1021/es990764p.

[17] Xing B. Sorption of naphthalene and phenanthrene by soil humic acids. *Environ Pollut.* 1997;96(3):357–362. doi:10.1016/S0269-7491(97)00041-1.

[18] Chiou CT, Kile DE, Rutherford DW, Sheng G, Boyd SA. Sorption of selected organic compounds from water to a peat soil and its humic acid and humin fractions: potential sources of sorption nonlinearity. *Environ Sci Technol.* 2000;34(7):1254–1258. doi:10.1021/es991114q.

[19] Zhang H, Selim HM. Sorption–desorption hysteresis of aromatic hydrocarbons in soils. *Soil Sci.* 2005;170(7):515–528. doi:10.1097/01.ss.0000169959.84438.6d.

[20] Wu S, Gschwend PM. Numerical modeling of sorption kinetics of organic compounds to soil and sediment particles. *Water Resour Res.* 1986;22(1):1–8. doi:10.1029/WR022i001p00001.

[21] Guo M, Chorover J. Transport and transformation of organic contaminants in soil–clay mineral systems. *Environ Sci Technol.* 2003;37(13):2760–2768. doi:10.1021/es026274m.

[22] Zhang Y, Li J, Chen H. Thermodynamics of pentachlorophenol sorption on natural sediments. *Chemosphere.* 2007;66(9):1745–1751. doi:10.1016/j.chemosphere.2006.07.062.

[23] Sheng G, Johnston CT, Teppen BJ, Boyd SA. Adsorption of dinitrophenol herbicides from water by montmorillonites modified with a cationic surfactant. *Environ Sci Technol.* 2001;35(22):4751–4756. doi:10.1021/es010916d.

[24] Wu L, Sun K, Jiang J, Pan Z, Xing B. Temperature dependence of sorption of organic compounds by soil humic acids. *Environ Sci Technol.* 2008;42(10):3619–3625. doi:10.1021/es702536j.

[25] Chiou CT, McGroddy SE, Kile DE. Partition characteristics of polycyclic aromatic hydrocarbons on natural sorbents. *Environ Sci Technol.* 1998;32(2):264–269. doi:10.1021/es970519z.

[26] Li J, Wu J, Yu H, Chen H. Effect of temperature on the sorption of pentachlorophenol by natural soils. *J Environ Sci (China).* 2008;20(2):224–230. doi:10.1016/S1001-0742(08)60034-2.

[27] Ho YS, McKay G. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *Can J Chem Eng.* 1998;76(4):822–827. doi:10.1002/cjce.5450760419.

[28] Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens Handlingar.* 1898;24(4):1–39.

[29] Freundlich H. Über die adsorption in lösungen. *Z Phys Chem.* 1906;57:385–470.

[30] Langmuir I. The adsorption of gases on plane surfaces of glass, mica, and platinum. *J Am Chem Soc.* 1918;40(9):1361–1403. doi:10.1021/ja02242a004.

[31] Weber WJ, DiGiano FA. *Process Dynamics in Environmental Systems.* New York: Wiley; 1996.

[32] Atkins PW, de Paula J. *Atkins' Physical Chemistry.* 9th ed. Oxford: Oxford University Press; 2010.

[33] Sparks DL, Jardine PM. Thermodynamics of soil potassium exchange. *Soil Sci Soc Am J.* 1981;45(6):1094–1099. doi:10.2136/sssaj1981.03615995004500060006x.

[34] Wu S, Gschwend PM. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ Sci Technol.* 1986;20(7):717–725. doi:10.1021/es00149a006.

[35] He Y, Xu J, Zhang Y, Jin J. Sorption–desorption behavior of pentachlorophenol on black carbon derived from rice straw. *Chemosphere.* 2008;70(5):859–865. doi:10.1016/j.chemosphere.2007.07.040.