Environmental and
Biogeochemical Processes

https://doi.org/10.48130/ebp-0026-0011

Original Research

Open Access

Size and aging-driven interactions between fluensulfone and PVC microplastics: the key role of fluorine-sensitive interactions

Aoze Li[1], Yiming Hou[2], Siwei Gao[2], Xiaoyun Li[1,2,3*], Shang Gao[1], Ben Philpot[1], Ian Eggleston[1] and Baoshan Xing[1*]

Received: 4 May 2026

Revised: 5 June 2026

Accepted: 3 July 2026

Published online: 20 August 2026

Abstract

Pesticides and microplastics (MPs) frequently co-occur in agricultural soils, yet their coupled sorption behavior remains insufficiently understood under environmentally relevant conditions. This study investigated the sorption, desorption, and co-adsorption of the fluorinated nematicide fluensulfone (FL) on pristine and aged polyvinyl chloride (PVC) MPs (1 and 150 μm), including soil–PVC systems. Aging, particularly for 1 μm MPs, accelerated sorption kinetics (equilibrium time reduced to as low as 4 h), increased sorption capacity (up to 1.5–2.0 fold), and enhanced desorption hysteresis (The hysteresis index [HI] increased from ≤ 0.08 to ≥ 0.39). These changes are attributed to increased surface polarity, porosity, and oxygen-containing functional groups that promote fluorine-sensitive interfacial interactions, likely associated with F···H–O hydrogen bonding. Environmental factors strongly influenced FL sorption: sorption increased with pH and Ca^{2+}, whereas Na^{+} and anions (NO_3^- > Cl^-) reduced sorption. Humic acid enhanced sorption with limited concentration dependence. In soil systems, soil organic matter dominated FL retention; however, aged 1 μm PVC increased total sorption by approximately 15%–25% and accounted for up to approximately 30%–35% of retained FL, with contributions increasing with PVC loading. Overall, aged fine PVC MPs act as supplementary sorbents that enhance the retention of fluorinated pesticides and may alter their environmental fate in agricultural soils.

Keywords: Aging microplastics, Fluorinated pesticides, Hydrogen bonding, Sorption behavior, Desorption hysteresis, Agricultural soils

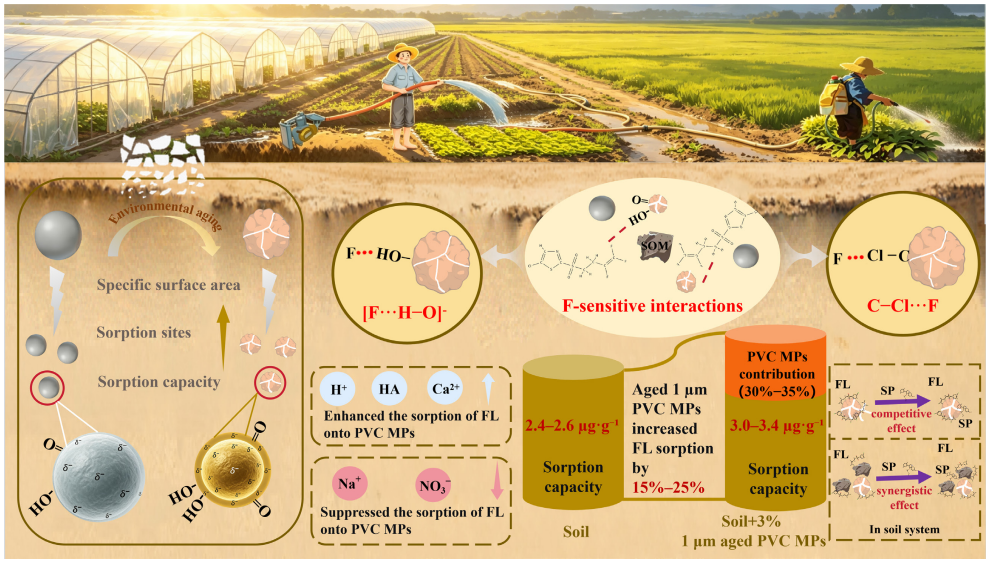
Highlights

- Aging enhances fluensulfone (FL) sorption and hysteresis on PVC MPs, especially for 1 μm MPs.
- FL sorption capacity increases with increasing pH via F-sensitive interactions, including F···H–O bond and F···Cl–C interactions.
- Ca^{2+} promotes sorption, while Na^{+}, Cl^- and NO_3^- reduce sorption of FL on PVC MPs.
- MPs increase FL retention in soil by providing additional sorption sites.
- Coexisting spirotetramat decreased FL sorption in the binary system, while it increased FL sorption in the soil–PVC MPs system.

* Correspondence: Xiaoyun Li (lxy518@snnu.edu.cn); Baoshan Xing (bx@umass.edu)
Full list of author information is available at the end of the article.

https://doi.org/10.48130/ebp-0026-0011

Graphical abstract



Introduction

Microplastics (MPs) and pesticides are two critical pollutants increasingly recognized for their co-occurrence in agricultural soils[1]. Globally, MPs in agricultural soils typically range from 0.3 to approximately 2.7×10^4 particles kg^{-1}, with an estimated global stock of 1.5–6.6 Mt, indicating that croplands are major terrestrial sinks for MPs[2,3]. MPs originate from the degradation of mulching films, greenhouse covers, irrigation infrastructure, and sludge application, and their abundance in facility-agriculture soils often far exceeds that in open-field systems, with greenhouse soils reported to contain 2,800–82,500 particles kg^{-1} in Hainan[4], and approximately 3.6×10^4 items kg^{-1} across multiple regions[5], compared with only 310–5,698 particles kg^{-1} in adjacent open-field soils[6]. In parallel, fluorine-containing pesticides have dominated the global agrochemical market in recent years due to their superior bioactivity and environmental stability, accounting for approximately 64% of all commercialized halogenated agrochemicals between 2016 and 2022[7]. Residues of halogenated agrochemicals such as fluensulfone (FL), fluopyram, and fludioxonil have been widely detected in both soils and crops, as confirmed by multiple field and market surveillance studies[8,9]. Structurally, the presence of fluorine imparts unique physicochemical properties such as high electronegativity and low polarizability, which enable these compounds to engage in specific noncovalent interactions (e.g., halogen bonding and hydrogen bonding) beyond conventional hydrophobic and van der Waals forces[10]. Thus, the simultaneous presence of MPs and fluorinated pesticides in soil raises new questions about their interactions and the subsequent implications for pesticide fate.

The sorption of pesticides onto MPs is generally understood as a multi-mechanistic process involving hydrophobic partitioning, electrostatic interactions, hydrogen bonding, and pore filling, with halogen-related interactions increasingly recognized for halogenated compounds[11,12]. For fluorinated pesticides, the presence of highly electronegative fluorine atoms may introduce additional noncovalent interactions, particularly F···H–O hydrogen bonding and possible fluorine-sensitive electrostatic interactions associated with polarized C–Cl environments (C–Cl···F), beyond conventional hydrophobic processes. Recent studies on fluorinated agrochemicals and per- and polyfluoroalkyl substances (PFAS) have demonstrated that F-mediated hydrogen bonding can coexist with hydrophobic partitioning and substantially enhance sorption onto mineral or polymeric surfaces[13]. It remains unclear whether sorption is governed by fluorine-sensitive interfacial interactions or nonspecific partitioning processes under soil-relevant conditions[14], enhanced surface hydrophilicity has been reported to reduce the adsorption of relatively polar pesticides on aged plastics[15]. As a result, the dominant sorption mechanisms of fluorinated pesticides on polyvinyl chloride (PVC) MPs—particularly under soil-relevant conditions—remain poorly constrained. It therefore remains unresolved whether the sorption of fluorinated pesticides such as FL on PVC MPs is governed primarily by fluorine-associated interactions (e.g., F···H–O hydrogen bonding and other polar interactions) or by nonspecific hydrophobic partitioning and pore-filling processes, and how these mechanisms are modulated by plastic aging and soil environmental factors.

Environmental conditions also play a key role in regulating pesticide–MPs interactions. Variations in pH can alter both pesticide speciation and MP surface charge, thereby shifting the relative contributions of electrostatic interactions and hydrogen bonding[16]. Likewise, cations such as Na^+ and Ca^{2+} may compete for sorption sites, with Ca^{2+} sometimes acting as a bridging agent, while anions (Cl^-, NO_3^-) may displace pesticides from active sites[17]. Furthermore, soil organic matter (SOM) introduces additional sorption domains, which may either outcompete MPs or promote co-sorption by forming organo–plastic aggregates[18]. The coexistence of other organic pollutants such as antibiotics, pharmaceuticals, or polycyclic aromatic hydrocarbons further complicates this picture, leading to competition for limited sorption sites or, in some cases, synergistic adsorption[19]. These complexities highlight an unresolved issue: do MPs act mainly as supplementary carriers in soil, enhancing pesticide retention, or do they reduce soil sorption capacity by competing with natural sorbents? In addition, natural organic matter such as humic acids and other high-molecular-weight compounds may exert significant influences on pesticide–MP interactions. Humic substances can coat MP surfaces, modify their hydrophobicity, and

introduce new binding sites, thus altering sorption capacities and mechanisms[20]. Similarly, the presence of co-contaminants such as other pesticides or antibiotics may cause competitive adsorption or promote multilayer sorption, further complicating the environmental behavior of fluorine-containing pesticides in soil–MP systems[21–24]. Given that MPs and these organics frequently coexist in agroecosystems, their combined effects warrant systematic investigation. Collectively, these uncertainties raise a critical knowledge gap as to whether the sorption of fluorine-containing pesticide contaminants on chlorine-rich MPs is governed by fluorine-specific hydrogen or halogen-related interactions, or remains dominated by nonspecific hydrophobic partitioning and pore-filling processes, particularly under environmentally relevant soil conditions.

Therefore, in this study, polyvinyl chloride (PVC) with two particle sizes (1 and 150 μm) in both pristine and aged forms was chosen as the model MPs because it is widely used in agricultural systems and its chlorine-rich backbone provides a chemically distinct surface for probing potential halogen- and fluorine-mediated interactions. FL was then employed as a representative fluorinated pesticide, and its behavior was systematically compared with that of a structurally distinct, non-fluorinated analogue, spirotetramat (SP) to mechanistically isolate fluorine-specific interactions from general sorption processes. A series of sorption experiments were designed to assess adsorption and desorption behavior of FL on PVC MPs in a soil system, while systematically evaluating the effects of pH and common inorganic ions (Na^+, Ca^{2+}, Cl^-, NO_3^-) on adsorption behavior. Beyond single-contaminant systems, competitive sorption experiments with FL and SP were conducted to identify differences in binding sites and cross-interactions between two structurally distinct fluorinated pesticides. Furthermore, soil–PVC co-sorption systems were established to simulate realistic agricultural conditions and to explore how MPs modify pesticide distribution between soil organic matter and plastic phases. The overarching goals of this study are: (1) to elucidate the effects of particle size, surface aging, and environmental factors in regulating fluorinated pesticides sorption on PVC MPs; (2) to determine whether MPs act as supplementary sorbents or competitors in soil matrices; and (3) to contrast the sorption behavior of fluorinated pesticide with other coexisting pesticide to isolate fluorine-specific interactions from general hydrophobic and pore-filling mechanisms. While previous studies have primarily focused on non-halogenated pesticides on common polymers such as PE or PS in simplified aqueous systems, this work advances mechanistic understanding by examining PVC, evaluating potential F···H–O and electrostatic interactions arising from polarization of C–Cl bonds, and incorporating soil coexisting conditions relevant to agricultural environments.

Materials and methods

Materials and reagents

Two size classes of polyvinyl chloride (PVC) MPs were employed in this study. Fine PVC particles with a mean diameter of 1 μm were obtained through online commercial procurement, whereas coarse PVC particles (150 μm) were supplied by Marginal Science. Spherical PVC MPs were selected to minimize variability associated with particle morphology and to facilitate systematic evaluation of particle-size and aging effects on sorption behavior. Although environmental PVC MPs are often irregularly shaped, spherical particles provide a reproducible model system that has been widely used in mechanistic sorption studies. To investigate pesticide–plastic interactions, two widely used commercial formulations were selected: Movento (from Bayer), containing 22.40% SP as the active ingredient, and Nimitz (from Adama Agricultural Solutions), formulated with 40% FL. Relevant physicochemical properties of both pesticides are provided in Supplementary Table S1 and Supplementary Fig. S1 of the Supplementary Information. Ethyl acetate, from Fisher Scientific (USA), was used only during sample extraction and HPLC analysis. All sorption, desorption, competitive sorption, and soil-system experiments were conducted in aqueous media. Ultrapure water was produced using a Milli-Q Advantage water purification system (Millipore, USA) and was used for the preparation of all aqueous solutions. A comprehensive summary of the physicochemical characteristics of the PVC MPs and pesticide compounds is presented in Supplementary Tables S1 and S2, respectively, in the Supplementary Information.

Agricultural soil was collected from the surface layer (0–20 cm) of the UMass Amherst Deerfield Research Farm, air-dried, sieved (< 2 mm), and characterized for basic physicochemical properties including pH, organic matter, cation exchange capacity, and texture. Deionized water (resistivity ≥ 18 MΩ cm) was used throughout all tests.

Simulation of environmental oxidation aging of PVC MPs

PVC MPs were artificially aged by oxidative treatment in 10 $g \cdot L^{-1}$ $K_2S_2O_8$ at 70 °C for 14 d following a modified method reported by He et al.[25]. The decomposition of persulfate generates reactive oxygen species that promote surface oxidation and the formation of oxygen-containing functional groups commonly observed on weathered plastics[26,27]. Previous studies have shown that this accelerated aging approach produces oxidation characteristics comparable to those of environmentally aged polymers and provides a reproducible method for investigating aging-induced changes in contaminant sorption behavior[28]. In particular, Doussiemo et al. reported that chemical oxidation treatments can generate substantial increases in carbonyl index and surface oxidation comparable to those observed in environmentally weathered MPs, further supporting the environmental relevance of this approach. After aging, the particles were repeatedly rinsed with deionized water until no residual oxidant was detected using a potassium iodide–starch indicator, then dried at 40 °C and stored in glass vials for subsequent experiments. A detailed justification of the aging protocol and its environmental relevance, including comparisons with natural weathering and alternative aging approaches, is provided in Supplementary Text S1.

Physicochemical properties of pristine and aged PVC MPs

We characterized both pristine and aged PVC MPs to identify physicochemical changes induced by oxidative aging. High-resolution scanning electron microscopy (SEM; FEI Magellan 400 XHR-SEM, USA) revealed surface morphological features, while nitrogen adsorption–desorption measurements using a Micromeritics TriStar II 3020 system enabled quantification of specific surface area and pore volume based on the Brunauer–Emmett–Teller (BET) theory. To examine chemical transformations on the PVC surface, we analyzed functional group evolution using Fourier-transform infrared spectroscopy (FTIR, PerkinElmer Spectrum One, USA) and further resolved surface elemental composition and chemical states via X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha, USA). We also assessed pH-dependent electrostatic properties by measuring zeta potential with a phase analysis light scattering analyzer (Brookhaven Instruments, USA). Together, these measurements provided the

https://doi.org/10.48130/ebp-0026-0011

physicochemical basis for interpreting particle-size and aging-dependent variations in pesticide sorption behavior. Detailed analytical procedures for each characterization technique are described in Supplementary Text S2.

Sorption–desorption behavior of FL on PVC MPs

The sorption behavior of FL on pristine and aged PVC MPs was investigated. For equilibrium isotherm experiments, initial FL concentrations ranged from 0.6 to 48 mg·L^{-1}, and based on the kinetic experiments, apparent sorption equilibrium was reached within 4–12 h depending on particle size and aging status (Supplementary Fig. S2). To ensure complete equilibration across all experimental conditions and maintain consistency among sorption, desorption, competitive sorption, and soil-system experiments, a contact time of 48 h was used for all subsequent equilibrium measurements. Aqueous FL concentrations were determined using high-performance liquid chromatography (HPLC) following standard sample pretreatment procedures (Supplementary Text S3). Calibration curves were established over the concentration range of 0.048–96 mg·L^{-1} (Supplementary Fig. S3). Sorption kinetics were evaluated using the pseudo-first-order (PFO), pseudo-second-order[15], Elovich[15], and intraparticle diffusion models[12], while equilibrium isotherms were described using Langmuir, Freundlich, and Dubinin–Radushkevich (DRM) models[12] to quantify sorption capacity and surface heterogeneity. Detailed model equations, parameter definitions, and fitted results are provided in Supplementary Text S4 and Supplementary Tables S3 and S4. All data were fitted using nonlinear regression and are reported as mean ± standard deviation of triplicate measurements. Desorption experiments were further conducted after sorption equilibrium was reached, and the release ratio (R_r) and hysteresis index (*HI*) were calculated to quantify desorption characteristics. The variation in sorption capacity between adsorption and desorption (ΔQ_e) was also determined, and detailed calculation methods are provided in Supplementary Text S4.

Effect of environmental conditions on FL sorption on PVC MPs

The influence of environmental factors on FL sorption onto PVC MPs was systematically investigated by varying solution chemistry. Specifically, the effects of: (i) ionic strength and composition (Na^+, Ca^{2+}, Cl^-, and NO_3^-); (ii) solution pH (4–12); and (iii) dissolved organic matter (humic acid, 0–20 mg·L^{-1}) were evaluated. Experimental details are provided in Supplementary Text S1. Changes in FL sorption under these conditions were quantified relative to control systems using the ΔQ_e parameter (Supplementary Text S4).

Co-adsorption behavior of FL and SP on pristine and aged PVC MPs in soil

To investigate interactions between coexisting pesticides, co-adsorption experiments were first conducted using FL and SP. In binary systems, SP was introduced at concentrations of 0.6 or 4.8 mg·L^{-1} into FL-containing solutions, followed by equilibration with PVC MPs under conditions identical to single-solute systems. Changes in FL sorption capacity in the presence of SP were quantified relative to FL-only controls. These experiments enabled evaluation of co-adsorption behavior and provided insight into potential synergistic or competitive interactions between the two pesticides.

Sorption of FL in soil–PVC coexistence systems was then examined to evaluate how MPs influence pesticide distribution under more realistic agricultural conditions. Specifically, 4.5 g of air-dried, sieved soil (≤ 2 mm) (more soil properties were in Supplementary Text S3 and Supplementary Fig. S4) was added to 30 mL of FL solution. PVC MPs (1 or 150 μm; pristine or aged) were added at a dosage of 1% w/w relative to soil to establish soil-MP coexistence conditions. The suspensions were shaken at 25 °C and 180 rpm for 7 d to reach apparent equilibrium. After equilibration, samples were centrifuged (3,000 rpm, 20 min), and the supernatants were filtered through 0.22 μm membranes for HPLC quantification of FL following the analytical procedures described in Supplementary Text S3. The amount of FL associated with MPs was calculated by subtracting soil-only controls from MP-containing treatments.

Competitive sorption in soil-PVC systems was evaluated by introducing SP at two environmentally relevant concentrations (0.6 and 4.8 mg·L^{-1}) into the FL solutions prior to mixing with soil and MPs. All other experimental conditions were identical to the single-solute tests. Following equilibration and HPLC analysis, the enhancement or suppression of FL sorption in the presence of SP was quantified by comparing the FL distribution between soil and MPs against the FL-only controls. All experiments were conducted in triplicate, with procedural blanks included to correct background adsorption and analytical losses.

Data analysis

Sorption capacity (Q, μg·g^{-1}) was calculated from the mass balance between initial and equilibrium solution concentrations. Changes in sorption induced by environmental factors or coexisting compounds were expressed as ΔQ, defined as the difference in equilibrium sorption capacity between treatment systems and their corresponding controls (Supplementarey Text S4 [Eq. 12]). Desorption behavior was evaluated using the release ratio (R_r) (Supplementarey Text S4 [Eq. 13]), calculated as the fraction of sorbed pesticide released during desorption relative to the initially adsorbed amount. Sorption irreversibility was further characterized by the hysteresis index (HI) (Supplementarey Text S4 [Eq. 14]), which reflects deviations between adsorption and desorption isotherms. In addition, the distribution coefficient (K_d, L·kg^{-1}) (Supplementarey Text S4 [Eq. 11]) was determined as the ratio of sorbed concentration to aqueous-phase concentration at equilibrium to describe pesticide partitioning between the solid and liquid phases.

All kinetic and isotherm parameters were obtained by nonlinear least-squares regression using Origin 2025 (OriginLab Inc., Northampton, MA, USA). Model performance was evaluated based on goodness-of-fit indicators and consistency with experimental trends. Detailed equations, parameter definitions, and calculation procedures for kinetic models, isotherm models, ΔQ, R_r, HI, and K_d are provided in Supplementarey Text S4 of the Supporting Information.

Results and discussion

Particle size-dependent physicochemical changes of pristine and aged PVC MPs

Environmental aging induced pronounced physical alterations in PVC MPs, with these effects becoming increasingly evident as particle size decreased, which has a profound influence on their interfacial behavior towards organic pollutants[29]. As presented in Fig. 1a–d, the surfaces of pristine PVC MPs appeared relatively smooth and compact; in contrast, aged MPs exhibited heterogeneous and damaged morphologies, with visible cracks, pits, and fragmented edges, attributable to oxidative aging effects. These morphological

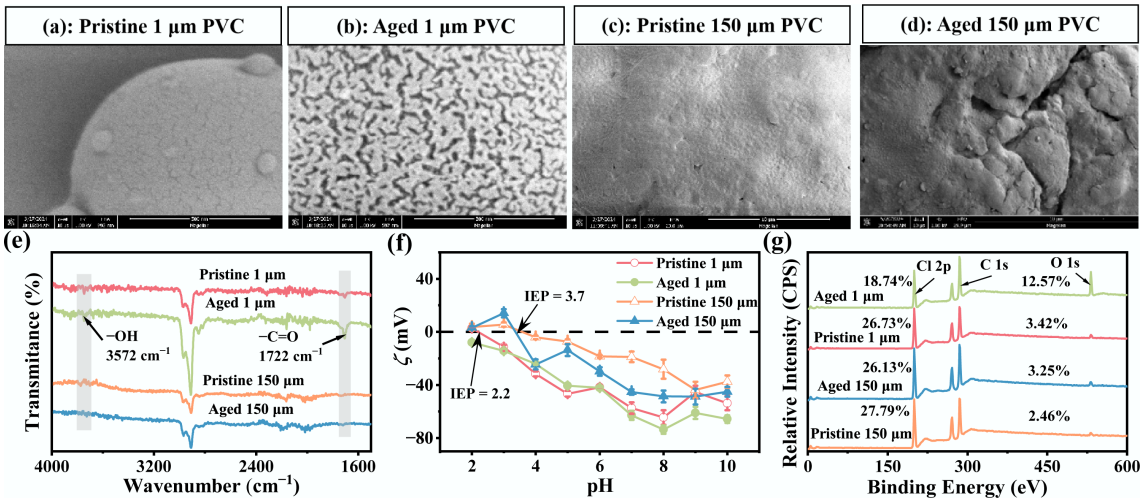


Fig. 1 Scanning electron microscopy images of (**a**) pristine 1 μm PVC, (**b**) aged 1 μm PVC, (**c**) pristine 150 μm PVC, and (**d**) aged 150 μm PVC. (**e**) FTIR spectra of pristine and aged PVC (1 and 150 μm). (**f**) Zeta potential showing the isoelectric point (IEP). (**g**) XPS wide-scan spectra.

transformations were accompanied by a noticeable increase in micro–mesoporous structures, as evidenced by BET results: the specific surface area increased from 4.10 to 4.50 $m^2 \cdot g^{-1}$ for 1 μm MPs and 0.114 to 0.747 $m^2 \cdot g^{-1}$ for 150 μm MPs, while the average pore size expanded from 11.63 to 13.85 nm (Supplementary Table S2). These structural changes indicate the formation of additional micro–mesoporous domains and more accessible diffusion pathways, particularly for smaller particles with higher surface curvature and reactivity. From a mechanistic perspective, such physical evolution is expected to increase the availability of sorption-accessible sites, reduce intraparticle diffusion resistance, and enhance mass transfer between the aqueous phase and the polymer interior. As a result, aged PVC MPs—especially at the 1 μm scale—are likely to exhibit accelerated sorption kinetics and increased apparent sorption capacity due to pore development and surface roughening alone, even in the absence of changes in surface chemistry.

In parallel, the chemical composition of PVC MPs surfaces also changed markedly depending on size and aging, as revealed by FTIR and XPS analyses. FTIR spectra revealed the emergence and intensification of characteristic absorption bands near 3,400 cm^{-1} (O–H stretching) and 1,730 cm^{-1} (C=O stretching) (Fig. 1e), confirming oxidative introduction of hydroxyl and carbonyl functionalities. XPS analysis corroborated this oxidation trend, showing an increase in the O/C ratio from 0.12 to 0.21 for 1 μm MPs and 0.11 to 0.19 for 150 μm MPs, together with binding-energy shifts of O 1s (531.3 to 532.1 eV) and Cl 2 $p_{3/2}$ (from 198.4 to 199.2 eV) (Fig. 1g; Supplementary Fig. S5), indicating partial dehydrochlorination and formation of oxygenated carbon species. The smaller 1 μm MPs experienced a more significant oxidation degree, consistent with their greater specific surface and susceptibility to radical attack. The introduction of these oxygen-containing groups also altered surface charge properties. ζ-potential measurements showed a clear shift toward more negative values after aging, from approximately −8.6 to −18.4 mV for 1 μm MPs and from −5.2 to −12.1 mV for 150 μm MPs at neutral pH (Fig. 1f), implying enhanced acidity and hydrophilicity of the aged surfaces. This increased electronegativity, combined with the development of mesopores and polar sites, substantially increases the capacity for specific interactions with polar or halogenated molecules. FTIR and XPS analyses verified the formation of hydroxyl, carbonyl, and other oxygenated groups during aging, alongside partial dechlorination (Fig. 1e), which collectively increased the polarity and electronegativity of PVC surfaces. The corresponding shift toward more negative ζ-potential values further supports the emergence of polar and acidic functional sites. These chemical and electrostatic changes are known to elevate the affinity of aged MPs toward polar and halogenated organic molecules by enabling hydrogen bonding, dipole–dipole attraction, and other specific interactions that are largely absent on pristine materials[14,15]. Given these textural and chemical evolutions, aged PVC, especially the 1 μm fraction, is expected to promote stronger interactions with FL. The introduction of oxygen-containing functional groups and the development of micro–mesoporous structures collectively increase surface polarity and heterogeneity, thereby promoting surface-site-controlled interactions with FL. Among these, fluorine-sensitive interfacial interactions—primarily associated with F···H–O hydrogen bonding—are likely to contribute to enhanced sorption. In addition, aging-induced modification of C–Cl environments may alter local interfacial polarity, giving rise to secondary Cl-associated interfacial effects rather than specific directional bonding. These enhanced specific interactions, together with expanded pore structures, are likely to modulate both sorption and desorption dynamics, as discussed in subsequent sections.

Aging clearly alters the adsorption–desorption behavior of FL on PVC MPs

Sorption kinetics of FL on pristine and aged PVC MPs

The sorption of FL onto PVC MPs exhibited a clear two-stage kinetic process across all treatments (Fig. 2a, b), characterized by a rapid initial sorption stage followed by a slower approach to equilibrium. Approximately 70%–80% of total sorption occurred within the first 2 h, after which the sorption rate progressively declined, and apparent equilibrium was reached within 8–12 h. This two-stage behavior is consistent with the widely reported sequence of rapid surface-site occupation followed by diffusion-controlled sorption within internal domains of porous or heterogeneous sorbents[11,12,30]. The rapid initial stage reflects sorption to readily accessible external sites, whereas the subsequent slower phase corresponds to diffusion of FL molecules into pores and newly formed aged-induced microdomains, as supported by intraparticle diffusion plots showing multi-linear characteristics

https://doi.org/10.48130/ebp-0026-0011

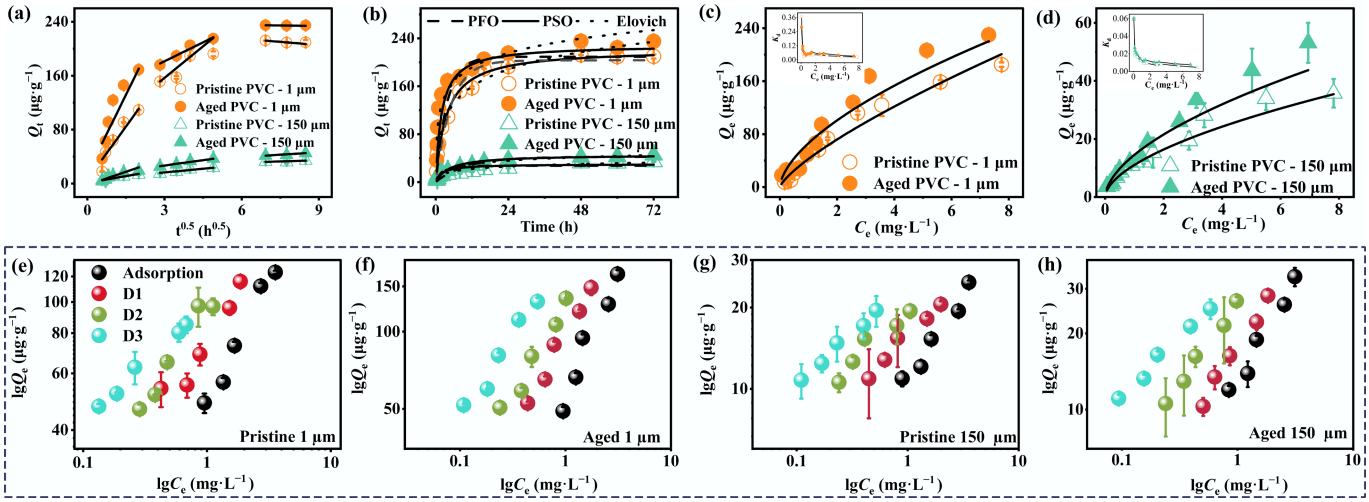


Fig. 2 (**a**) Sorption kinetics of FL onto PVC fitted using the intraparticle diffusion model, and (**b**) the pseudo-first-order, pseudo-second-order, and Elovich models. Adsorption isotherms of FL onto PVC based on Freundlich model fitting, along with distribution coefficient (K_d) values for (**c**) 1 μm PVC MPs and (**d**) 150 μm PVC MPs. Adsorption and desorption behavior of FL on (**e**) pristine 1 μm, (**f**) aged 1 μm, (**g**) pristine 150 μm, and (**h**) aged 150 μm PVC. The equilibrium time for all adsorption and desorption processes was 48 h. The initial concentration range for sorption isotherms was 0.24–9.6 mg·L^{-1}, and the temperature was maintained at 25 ± 1 °C.

(Supplementary Fig. S6). Both particle size and surface aging exerted pronounced effects on sorption kinetics. For the 1 μm PVC MPs, sorption data were best described by the pseudo-second-order (PSO) model (r_{adj}^2 > 0.97; Supplementary Table S3), suggesting that sorption rates were strongly controlled by surface reaction processes involving specific binding sites. In contrast, sorption on the 150 μm particles was better fitted by the pseudo-first-order (PFO) model (r_{adj}^2 > 0.96), indicating that physical sorption and diffusion-related processes dominated on larger, less reactive particles. These differences highlight a particle-size-dependent shift in the controlling sorption mechanism.

Oxidative aging markedly accelerated FL sorption for both 1 and 150 μm particle sizes, as reflected by higher initial sorption rates in the Elovich model and steeper early-stage slopes in intraparticle diffusion analyses (Supplementary Fig. S6b, S6c). The acceleration of FL sorption induced by oxidative aging can be directly linked to the particle-size-dependent physicochemical transformations. For the 1 μm PVC MPs, aging produced pronounced surface roughening, extensive crack formation, and a substantial increase in accessible micro–mesoporous domains, which collectively reduced diffusion resistance and increased the availability of high-energy surface sites. These structural features are consistent with the observed dominance of pseudo-second-order kinetics and the markedly enhanced initial sorption rates, indicating that surface-site-mediated processes became increasingly rate-controlling on aged fine particles. In contrast, although aging also increased surface area and pore volume for the 150 μm MPs, these changes were less extensive and primarily manifested as moderate pore development rather than pervasive surface restructuring. As a result, sorption on the larger particles remained better described by PFO kinetics, reflecting continued control by diffusion and physical partitioning processes. This parallel between size-dependent physical evolution and kinetic behavior demonstrates that oxidative aging amplifies sorption kinetics by restructuring surface-accessible domains on small PVC MPs, whereas its impact on larger particles is comparatively limited. The dominance of PSO kinetics for aged 1 μm PVC MPs, together with elevated Elovich initial sorption rates, suggests that FL sorption is not governed solely by diffusion or hydrophobic partitioning, but involves surface-reaction-controlled processes associated with specific binding sites. Given the oxidative introduction of hydroxyl and carbonyl groups on aged PVC surfaces. These kinetic features suggest that sorption is increasingly governed by surface-site-controlled processes rather than purely diffusion-limited partitioning. Such behavior is consistent with the involvement of heterogeneous interfacial domains, potentially associated with fluorine-sensitive interactions on aged PVC surfaces.

Isothermal adsorption of FL on pristine and aged PVC MPs

Oxidative aging exerted a consistent and pronounced enhancement on the equilibrium sorption behavior of FL on PVC MPs, as evidenced by increases in both maximum sorption capacity and sorption affinity across particle sizes (Fig. 2c, d; Supplementary Table S4). For 1 μm PVC MPs, Langmuir maximum sorption capacity (q_0) increased from 291.55 μg·g^{-1} for pristine particles to 344.25 μg·g^{-1} after aging, corresponding to an enhancement of approximately 23% (Supplementary Fig. S7). In parallel, the Freundlich affinity coefficient (K_f) increased from 43.47 to 66.35, while the Freundlich nonlinearity parameter (n) decreased from 0.77 to 0.60, indicating both stronger sorption and increased heterogeneity of high-energy binding sites. Similar but less pronounced trends were observed for 150 μm PVC MPs, where q_0 increased from 26.37 to 34.00 μg·g^{-1} and K_f increased from 11.04 to 14.50 following aging, whereas n remained nearly constant (approximately 0.57). These systematic changes directly reflect the aging-induced physicochemical transformations described in the above section. Oxidative aging generated additional micro–mesoporous domains and introduced oxygen-containing functional groups (–OH and –C=O), thereby increasing surface polarity and energetic heterogeneity. Such modifications expand the population of high-affinity sorption sites and shift FL uptake away from simple partitioning toward site-specific interactions. Importantly, the magnitude of aging-induced enhancement was substantially greater for 1 μm MPs than for 150 μm MPs, demonstrating that smaller particles—owing to their higher surface reactivity, greater degree of oxidation, and more extensive pore development—respond more strongly to aging in terms of both sorption capacity and affinity.

The equilibrium isotherms of FL on all PVC MPs exhibited pronounced nonlinearity (Fig. 2c, d), characterized by rapid sorption at low equilibrium concentrations followed by gradual saturation at higher concentrations. Such behavior is indicative of heterogeneous sorption domains with a wide distribution of site energies, a feature commonly observed for polar organic contaminants interacting with aged polymeric surfaces[12,14]. Particle size further modulated this nonlinearity. Across both pristine and aged materials, 1 μm PVC MPs consistently displayed higher sorption capacities and stronger nonlinearity (lower n values) than their 150 μm counterparts. This size-dependent behavior is consistent with BET results (Supplementary Table S2), which show that smaller particles possess higher accessible surface area, more developed mesoporous networks, and shorter diffusion distances. These structural features increase the availability of both external and internal high-energy sorption domains, resulting in elevated K_f values and more favorable sorption at low concentrations. Collectively, the combined effects of aging and particle size indicate that equilibrium sorption of FL on PVC MPs is controlled by heterogeneous, high-affinity domains whose abundance and energetic distribution are markedly amplified by oxidative aging, particularly for smaller particles. The pronounced increases in sorption affinity and nonlinearity further suggest that FL sorption is driven primarily by oxidation-enabled, site-specific interactions rather than by nonspecific hydrophobic partitioning into the polymer matrix. Such behavior implies preferential sorption onto a limited number of energetically favorable sites instead of uniform distribution within the PVC phase.

The enhanced nonlinearity and increased affinity indicate the presence of heterogeneous, high-energy sorption domains. These domains are likely associated with fluorine-sensitive interfacial interactions, arising from the combined effects of oxygen-containing functional groups and increased surface polarity following aging. The preferential occupation of these sites is consistent with the observed enhancement in isotherm nonlinearity (lower n values) and elevated Freundlich affinity coefficients, especially for aged 1 μm PVC MPs.

Desorption hysteresis behavior of FL on pristine and aged PVC MPs

The kinetic signatures of surface-reaction control and the strongly nonlinear, high-affinity isotherms observed on aged PVC MPs collectively suggest that FL sorption may involve specific, energetically strong interactions beyond simple physical partitioning. Desorption experiments were therefore conducted to evaluate the reversibility of these interactions and to assess whether aging-induced binding domains give rise to sorption hysteresis. Desorption results revealed that FL sorption on both pristine and aged PVC MPs exhibited measurable hysteresis, with discernible differences depending on particle size and aging state (Fig. 2e, f). For pristine MPs of both sizes, a substantial fraction of sorbed FL was released upon transfer to clean background solution, yielding relatively high release ratios ($R_r \approx$ 0.14–0.28) and low hysteresis indices (HI ≤ 0.15; Supplementary Table S5). These results indicate that, although minor hysteresis was present, FL sorption on unaged PVC surfaces remained largely reversible and was dominated by weak physisorption and limited pore entrapment, consistent with the low surface polarity and scarcity of high-affinity sites on pristine PVC (Fig. 1; Supplementary Table S2). Aging led to a moderate increase in sorption hysteresis, as reflected by slightly reduced R_r values and elevated HI values (Supplementary Table S5), suggesting strengthened retention of FL on oxidized surfaces. However, the relatively small magnitude of this increase indicates that aging enhances binding strength without fundamentally altering the overall reversibility of the sorption process. Similar patterns of weak-to-moderate hysteresis have been reported for pesticide–MPs systems where specific interactions are present but do not fully suppress desorption[12,14].

In contrast, aged PVC MPs exhibited moderately reduced desorption compared with their pristine counterparts, with the effect being more evident for the 1 μm fraction (Fig. 2e, f). Aging resulted in lower release ratios and elevated hysteresis indices (Supplementary Table S5), indicating strengthened retention of FL on oxidized surfaces, although complete irreversibility was not observed. These desorption patterns provide mechanistic validation of the kinetic and isotherm results, which collectively suggested the involvement of surface-site-controlled interactions beyond simple physical partitioning. The enhanced hysteresis upon aging is consistent with the physicochemical transformations, including increased surface roughness, development of micro–mesoporous structures, and enrichment of oxygen-containing functional groups (–OH, –C–O–, and –C=O) revealed by SEM, BET, FTIR, and XPS analyses (Fig. 1). From a mechanistic perspective, these features generate localized, high-affinity sorption domains that stabilize FL binding and partially restrict desorption mobility. In particular, oxygen-containing groups introduced during aging can serve as hydrogen-bond donors or acceptors, facilitating fluorine-sensitive interactions such as F···H–O bonding, while aging-induced modification of C–Cl environments may also introduce Cl-associated interfacial interactions. The persistence of FL on aged surfaces during desorption therefore supports the hypothesis, proposed in the above sorption kinetics and Isothermal adsorption part, that these specific interactions contribute to stronger binding at a subset of surface sites rather than uniform polymer-phase partitioning.

Entrapment within newly formed micro–mesopores likely provides an additional, complementary contribution to hysteresis by imposing diffusion limitations, particularly for the 1 μm MPs with more accessible internal domains. Collectively, the desorption results confirm that oxidative aging enhances the contribution of specific, high-affinity surface interactions to FL sorption on PVC MPs, while still retaining a largely reversible character. This moderate but consistent increase in hysteresis demonstrates that aging amplifies interaction strength without fully suppressing desorption, thereby reinforcing the particle-size-dependent sorption mechanisms inferred from kinetic and isotherm analyses.

Effects of environmental factors on sorption behavior of FL on PVC MPs

Effect of pH

Solution pH exerted a pronounced and systematic influence on FL sorption on both pristine and aged PVC MPs (Fig. 3a–c). Contrary to the commonly reported behavior for pesticide–microplastic systems, FL sorption increased progressively with increasing pH across the examined range (pH 4–12). For pristine 1 μm PVC MPs, the equilibrium sorption capacity (Q_e) increased from 161.9 μg·g^{-1} at pH 4 to 307.9 μg·g^{-1} at pH 12, representing an increase of approximately 90%. A similar but more pronounced trend was observed for aged 1 μm MPs, where Q_e increased from 199.8 to 377.9 μg·g^{-1} over the same pH range. Particle size strongly modulated this pH response. For pristine 150 μm PVC MPs, Q_e increased from 27.6 μg·g^{-1} at pH 4 to 84.9 μg·g^{-1} at pH 12, whereas aged 150 μm MPs exhibited an increase from 38.0 to 93.2 μg·g^{-1}, indicating that pH-enhanced sorption occurred for both size fractions but was substantially amplified for smaller particles and aged surfaces. The pH-dependent enhancement in sorption was

https://doi.org/10.48130/ebp-0026-0011

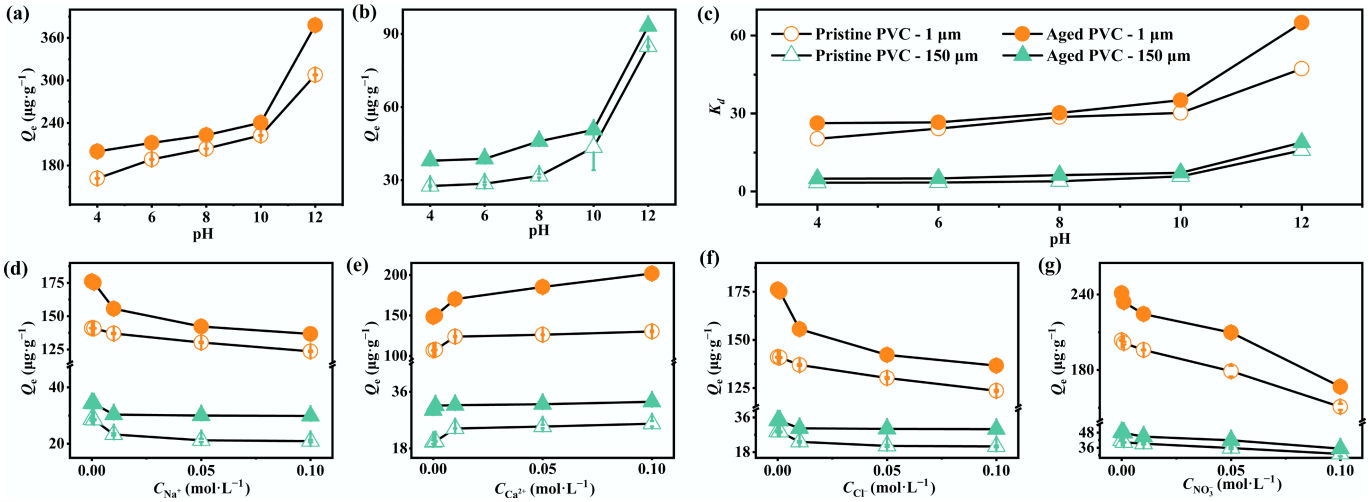


Fig. 3 Effect of pH on FL sorption by pristine and aged PVC MPs with (**a**) 1 μm, and (**b**) 150 μm particle size, and (**c**) corresponding distribution coefficients (K_d) as a function of pH. Effect of ionic conditions on FL sorption, including (**d**) Na^+, (**e**) Ca^{2+}, (**f**) Cl^-, and (**g**) NO_3^-.

further corroborated by changes in the distribution coefficient (K_d) (Fig. 3c). For pristine 1 μm MPs, K_d increased from 20.3 L·kg^{-1} at pH 4 to 47.2 L·kg^{-1} at pH 12, while aged 1 μm MPs showed an even stronger increase from 26.3 to 64.9 L·kg^{-1}. In contrast, pristine 150 μm MPs exhibited a more moderate increase in K_d from 3.36 to 15.84 L·kg^{-1}, and aged 150 μm MPs from 4.94 to 18.87 L·kg^{-1}. The concurrent increase in both Q_e and K_d with rising pH demonstrates that elevated pH enhances the affinity and partitioning of FL onto PVC MPs rather than suppressing sorption.

In most reported MPs–pesticide systems, increasing solution pH suppresses sorption due to enhanced surface deprotonation, increased electrostatic repulsion, and weakened hydrogen bonding, particularly when sorption is dominated by nonspecific polar interactions rather than hydrophobic partitioning[16,31]. Under such conditions, rising pH typically renders MP surfaces more negatively charged and hydrophilic, thereby reducing their affinity for organic contaminants. However, the FL–PVC system investigated here exhibits a fundamentally different response, as evidenced by the monotonic increases in both sorption capacity and K_d with increasing pH across all particle sizes and aging states. This anomalous pH-enhanced sorption cannot be attributed to changes in FL speciation, because FL remains predominantly in a neutral molecular form throughout the investigated pH range (pH 4–12; Supplementary Fig. S1). Instead, the increasing K_d values with rising pH provide direct quantitative evidence that elevated pH strengthens the affinity of FL for PVC surfaces rather than weakening it. For example, K_d for pristine 1 μm PVC MPs increased from 20.3 to 47.2 L·kg^{-1}, while aged 1 μm MPs exhibited an even more pronounced increase from 26.3 to 64.9 L·kg^{-1} as pH increased from 4 to 12. Similar but weaker trends were observed for 150 μm MPs, indicating that the pH response is intrinsic to the FL–PVC interaction but amplified by small particle size and surface aging. Mechanistically, this behavior reflects the dominance of specific, fluorine-sensitive surface interactions that become increasingly effective under alkaline conditions. As pH increases, deprotonation of aging-induced oxygen-containing functional groups (–OH and –C=O) on PVC surfaces enhances their ability to participate in directional hydrogen bonding with the fluorinated moieties of FL. These trends suggest that sorption is increasingly dominated by fluorine-sensitive interfacial interactions under alkaline conditions. In parallel, pH-induced changes in surface chemistry may further modulate C–Cl-associated interfacial properties, contributing to the overall enhancement in sorption. These interaction pathways are consistent with the observed increases in sorption nonlinearity and affinity (higher K_d) at elevated pH.

The particle-size dependence of the pH effect further supports this mechanism. Smaller PVC MPs, particularly the aged 1 μm fraction, exhibited the steepest increases in both Q_e and K_d with pH, reflecting their higher density of accessible functional groups, greater surface heterogeneity, and shorter diffusion pathways. Aging amplifies these effects by generating heterogeneous, high-energy binding domains that persist under alkaline conditions, allowing specific interactions to outweigh the repulsive influence of increased surface electronegativity. Collectively, these results demonstrate that FL sorption on PVC MPs is governed by interaction mechanisms fundamentally distinct from those controlling most pesticide–MP systems, with fluorine-sensitive, surface-specific interactions becoming increasingly dominant at elevated pH.

Effect of cations and anions on sorption behavior

Monovalent and divalent cations exerted fundamentally different, concentration-dependent effects on FL sorption on PVC MPs (Fig. 3a–d). Increasing concentrations of the monovalent cation Na^+ consistently suppressed FL sorption across all particle sizes and aging states. For aged 1 μm PVC MPs, the equilibrium sorption capacity (Q_e) decreased from 177.0 μg·g^{-1} at 0 mM Na^+ to 136.7 μg·g^{-1} at 0.1 mM, corresponding to a reduction of approximately 23%. A similar inhibitory trend was observed for pristine 1 μm MPs, where Q_e declined from 147.8 to 123.6 μg·g^{-1} (16% decrease). The suppression effect of Na^+ was even more pronounced for larger particles: for pristine 150 μm MPs, Q_e decreased from 35.5 to 20.9 μg·g^{-1} (41% decrease), while aged 150 μm MPs showed a reduction from 38.3 to 29.9 μg·g^{-1} (22% decrease). These results indicate that increasing Na^+ concentration weakens FL–PVC interactions primarily through ionic strength effects, including compression of the electrical double layer and disruption of interfacial hydrogen bonding, without directly contributing to surface coordination. In contrast, increasing concentrations of the divalent cation Ca^{2+} markedly enhanced FL sorption on PVC MPs. For aged 1 μm MPs, Q_e increased from 149.8 μg·g^{-1} in the absence of Ca^{2+} to 201.8 μg·g^{-1} at 0.1 mM Ca^{2+}, representing an

increase of approximately 35%. Pristine 1 μm MPs exhibited a comparable enhancement, with Q_e rising from 97.8 to 130.3 μg·g^{-1} (33% increase). Although the absolute sorption capacities of 150 μm MPs were lower, Ca^{2+} still promoted FL sorption: Q_e increased from 20.2 to 25.8 μg·g^{-1} for pristine 150 μm and from 29.2 to 32.8 μg·g^{-1} for aged 150 μm as Ca^{2+} concentration increased to 0.1 mM. This opposite response to Ca^{2+} highlights a mechanism distinct from simple ionic screening. The strong affinity of Ca^{2+} for aging-induced oxygen-containing functional groups may facilitate cation-bridging interactions that stabilize FL molecules at the PVC surface. In addition, direct coordination between Ca^{2+} and oxygen-bearing groups in FL (e.g., sulfonyl and carbonyl functionalities) cannot be excluded. Nevertheless, the stronger Ca^{2+} effect observed for aged PVC relative to pristine PVC suggests that interactions involving oxidation-induced surface functional groups are likely the predominant contributor to the enhanced sorption. Such Ca^{2+}-mediated coordination may enhance local ordering and promote fluorine-sensitive interactions, primarily through F···H–O hydrogen bonding and polar interfacial stabilization, thereby increasing the effective density of high-affinity sorption domains.

Anionic species also modulated FL sorption in an ion-specific manner (Fig. 3e–g). Increasing concentrations of NO_3^- caused a substantial decrease in FL sorption across all PVC MPs. For aged 1 μm MPs, Q_e decreased from 245.1 μg·g^{-1} at 0 mM NO_3^- to 186.8 μg·g^{-1} at 0.1 mM, corresponding to a 24% reduction. Pristine 1 μm MPs showed an even stronger decrease, from 203.6 to 150.8 μg·g^{-1} (26% reduction). The suppressive effect of NO_3^- was particularly pronounced for 150 μm MPs: Q_e decreased from 50.6 to 25.4 μg·g^{-1} (approximately 50% reduction) for pristine 150 μm MPs and from 42.9 to 15.2 μg·g^{-1} (approximately 65% reduction) for aged 150 μm MPs. By comparison, Cl^- exerted a weaker inhibitory effect that closely resembled the Na^+ background electrolyte trend. For aged 1 μm MPs, Q_e decreased from 177.0 to 136.7 μg·g^{-1} as Cl^- concentration increased to 0.1 mM, whereas changes for other particle sizes were moderate. This contrast between NO_3^- and Cl^- suggests that anion effects are governed not solely by charge but by ion-specific hydration and solvation properties. Nitrate, with its larger hydration shell and higher dipole moment, more effectively disrupts interfacial water networks that stabilize hydrogen- and halogen-bonding interactions at oxidized PVC surfaces, leading to stronger suppression of FL sorption. Despite the contrasting effects of different ionic species, aged PVC MPs consistently retained higher FL sorption than pristine MPs under all ionic conditions examined. This persistence underscores the dominant role of aging-induced heterogeneous, polar, and fluorine-sensitive binding domains in controlling FL sorption, even in the presence of elevated ionic strength and competitive solvation.

Effect of coexisting compound

Humic acid (HA) is a ubiquitous component of natural organic matter in soils and aquatic systems and is therefore expected to coexist with both MPs and pesticides under environmentally relevant conditions. Evaluating the influence of HA is essential for assessing whether FL sorption on PVC MPs is altered in realistic matrices. As shown in Fig. 4a, the addition of HA consistently enhanced FL sorption on both pristine and aged PVC MPs compared with HA-free systems, as quantitatively supported by positive changes in sorption capacity (ΔQ_e, Supplementary Text S4) across all experimental treatments. Notably, however, FL sorption exhibited only limited variation across the examined HA concentration range (0–20 mg·L^{-1}, Supplementary Text S3), indicating that the effect of HA was not strongly concentration dependent once present in the system. This behavior, coupled with the high surface area and porosity of aged PVCs (e.g., 4.50 m^2·g^{-1} and 0.014 cm^3·g^{-1} for aged 1 μm, Supplementary Table S2), suggests that HA does not act primarily through progressive surface coverage or pore blockage. Instead, even minimal HA appears sufficient to modify interfacial properties and promote FL retention. Mechanistically, HA molecules adsorbed onto PVC surfaces may introduce additional polar functional groups, analogous to the aging process, which enriched surface O/C ratios (e.g., from 0.12 to 0.21 for 1 μm MPs, as revealed by XPS), and reorganize interfacial water structure, thereby facilitating fluorine-sensitive or polar interactions between FL and the sorbent. Such HA-mediated interfacial modification enhances access to high-affinity binding domains, as supported by the higher Freundlich K_f values of aged MPs (e.g., 66.35 vs 43.47 for pristine 1 μm, Supplementary Table S4), without requiring extensive HA accumulation. The relatively weak concentration dependence further implies that these interfacial effects reach saturation rapidly, and that additional HA contributes little to further enhancement. Across all HA concentrations, aged PVC MPs consistently exhibited higher FL sorption than pristine materials, as evidenced by their higher kinetic and equilibrium sorption capacities (e.g., $q_{e,cal}$: 209.16 vs 203.17 μg·g^{-1}; q_0: 344.25 vs 291.55 μg·g^{-1} for 1 μm PVC, Supplementary Tables S3 and S4), indicating that aging-generated heterogeneous, high-affinity domains remain the dominant contributors to FL uptake even in the presence of natural organic matter. Collectively, these results demonstrate that HA acts as an interfacial modifier that promotes FL sorption on PVC MPs, rather than as a simple blocking agent or a concentration-controlled competitor.

In natural and agricultural environments, pesticides rarely occur in isolation; instead, multiple organic contaminants frequently coexist and compete for shared sorption domains on environmental matrices. To assess such multisolute interactions, the influence of the non-fluorinated pesticide SP on FL sorption by pristine and aged PVC MPs was systematically evaluated in this study. As shown in Fig. 4b–d, the presence of SP generally reduced FL sorption across the investigated concentration range, indicating that competitive effects dominated the overall interaction. At low FL concentrations, however, the suppressive effect of SP was relatively weak and, in a few cases, a slight enhancement was observed. For example, on pristine 1 μm PVC MPs, FL sorption at 0.48 mg·L^{-1} increased from 10.16 μg·g^{-1} (SP-free) to 12.57 μg·g^{-1} in the presence of 0.6 mg·L^{-1} SP, corresponding to an increase of approximately 24%. Similar minor deviations were observed at other low-concentration points, whereas the overall trend remained suppressive. These limited increases suggest that, at trace FL levels, partial occupation of low-affinity domains by SP may induce interfacial reorganization that transiently enhances the accessibility of higher-energy polar sites. As FL concentration increased, the competitive nature of SP became increasingly evident. At 9.6 mg·L^{-1} FL on pristine 1 μm, Q_e decreased from 184.9 μg·g^{-1} (SP-free) to 107.4 μg·g^{-1} with 0.6 mg·L^{-1} SP and further to 102.5 μg·g^{-1} with 4.8 mg·L^{-1} SP, corresponding to an overall reduction of about 45%. A similar concentration-dependent suppression was observed for aged 1 μm MPs, where Q_e declined from 229.8 to 165.5 and 151.0 μg·g^{-1} in the presence of 0.6 and 4.8 mg·L^{-1} SP, respectively (Supplementary Fig. S8). For 150 μm particles, although absolute sorption capacities were lower, SP-induced suppression was even more pronounced, with reductions exceeding 30%–40% at high FL concentrations. Mechanistically, these results indicate that SP primarily suppresses FL sorption through surface site competition and pore domain occupation rather than by directly displacing fluorine-specific binding configurations. The persistence of nonlinear FL isotherms under

https://doi.org/10.48130/ebp-0026-0011

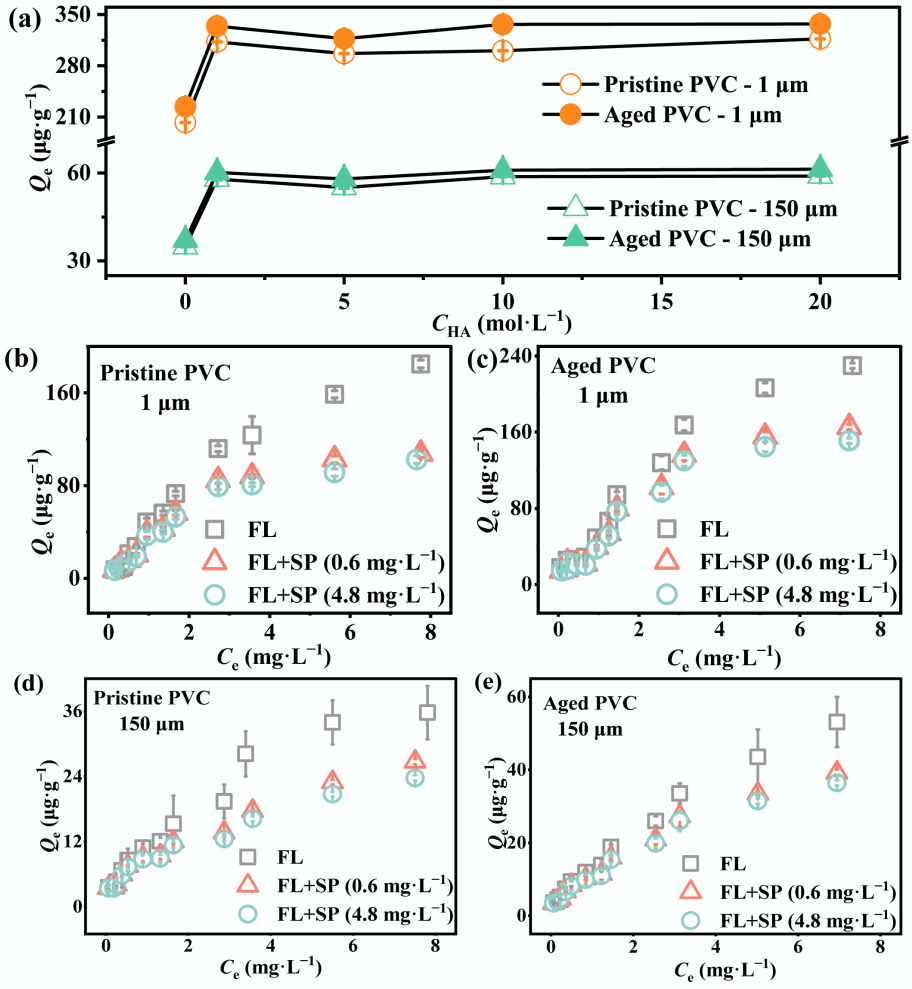


Fig. 4 Effects of humic acid (HA) and spirotetramat (SP) on FL sorption onto PVC MPs. (**a**) Effect of HA concentration. FL sorption in the absence and the presence of 0.6 and 4.8 mg·L^{-1} SP onto pristine (**b**) 1 μm PVC, (**c**) aged 1 μm PVC, (**d**) pristine 150 μm PVC, and (**e**) aged 150 μm PVC.

competitive conditions (Supplementary Fig. S9) suggests that high-affinity polar domains remain operative but become increasingly masked or less accessible as SP coverage increases. The weak or slightly positive deviations observed at low FL concentrations therefore represent a secondary, interfacial reorganization effect rather than true cooperative sorption. Similar concentration-dependent competitive sorption behaviors have been reported for mixed organic contaminants interacting with MPs surfaces[22,23].

The influence of PVC MPs on the sorption behavior of FL in soil system

Effect of PVC MPs on sorption behavior of FL in soil system

In soil–PVC coexistence systems, the introduction of PVC MPs resulted in a measurable increase in total FL retention relative to soil-only controls, as reflected by positive values of ΔQ (Fig. 5a). In the absence of PVC, soil alone removed approximately 2.4–2.6 μg·g^{-1} of FL. When aged 1 μm PVC MPs were added, the net sorption increment (ΔQ) increased systematically with PVC loading. At 1% PVC addition, ΔQ increased by approximately 0.3–0.4 μg·g^{-1}, while at 3% PVC addition, ΔQ reached approximately 0.6–0.8 μg·g^{-1}, corresponding to an enhancement of approximately 12%–33% relative to soil-only systems relative to soil-only systems. In contrast, pristine PVC MPs induced a much smaller ΔQ under the same conditions, indicating that aging substantially amplified the contribution of PVC to system-level FL retention. The magnitude of ΔQ also exhibited a strong particle-size dependence. Aged 1 μm PVC MPs consistently generated higher ΔQ values than aged 150 μm MPs at equivalent mass fractions, confirming that fine particles with higher surface reactivity and greater accessibility of polar domains play a disproportionately important role in enhancing FL sorption in soil matrices (Fig. 5a). Notably, ΔQ values remained positive across all treatments, indicating that the presence of PVC MPs enhanced overall FL retention rather than displacing FL from soil sorption sites. Partitioning analysis further elucidated how FL was distributed between soil and PVC phases, as quantified by the *p* value (Fig. 6). In soil systems amended with pristine 1 μm PVC MPs, only approximately 18%–22% of sorbed FL was associated with the plastic phase, with the majority retained by soil organic matter. In contrast, aged 1 μm PVC MPs accounted for approximately 30%–35% of total FL sorption under identical conditions, representing an increase of approximately 10–15 percentage points relative to pristine PVC. Aged 150 μm PVC MPs exhibited a smaller contribution, with *p* values of approximately 15%–20%, highlighting the combined influence of particle size and aging on phase-specific sorption behavior.

Taken together, the ΔQ and *p* value analyses demonstrate that aged, fine PVC MPs function as supplementary sorbents rather

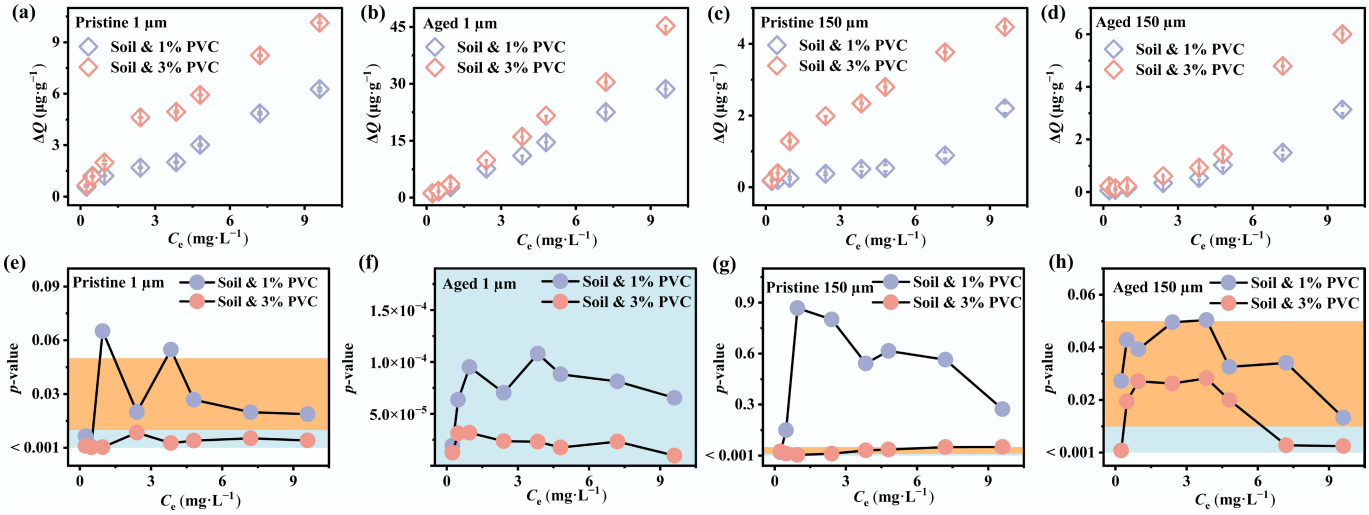


Fig. 5 Effect of PVC addition on FL sorption behavior in soil-PVC MPs system. Sorption enhancement of FL in soil with 1% and 3% additions of (**a**) pristine 1 μm PVC, (**b**) aged 1 μm PVC, (**c**) pristine 150 μm PVC, and (**d**) aged 150 μm PVC. (**e**)–(**h**) Statistical significance of sorption enhancement under the same conditions (Student's *t*-test). ΔQ_e represents the change in sorption capacity before and after PVC addition ($\Delta Q_e = Q_{e,\,before} - Q_{e,\,after}$). $p < 0.05$ indicates significance, and $p < 0.01$ indicates extreme significance.

than competitors to soil organic matter. While SOM remains the dominant sorbent for FL in soil systems, aged PVC introduces additional polar and halogen-sensitive binding domains that are not fully occupied by soil sorption sites. As a result, the incorporation of aged PVC MPs increases total system-level FL retention without measurably reducing the soil-associated fraction, thereby enhancing the overall capacity of soil–plastic systems to retain fluorinated pesticides.

Effect of PVC MPs on co-adsorption behavior of FL and SP in soil system

To further evaluate multisolute interactions under soil-relevant conditions, co-adsorption experiments were conducted to quantify how the coexisting pesticide SP modulates FL retention on PVC MPs. As shown in Fig. 6a–c, the presence of SP led to a measurable increase in FL sorption on PVC MPs, with the magnitude of enhancement depending strongly on both SP concentration and particle size. These results indicate that SP does not simply compete with FL for identical binding sites but instead alters the interfacial sorption environment in a manner that promotes FL retention. For aged 1 μm PVC MPs, co-adsorption effects were particularly pronounced. At an SP concentration of 0.6 mg·L^{-1}, FL sorption increased by approximately 0.20–0.30 μg·g^{-1}, corresponding to a relative enhancement of approximately 18%–22% compared with FL-only systems. Increasing SP concentration to 4.8 mg·L^{-1} further elevated FL sorption by approximately 0.35–0.50 μg·g^{-1}, yielding an overall enhancement of approximately 28%–32%. In contrast, aged 150 μm PVC MPs exhibited substantially weaker co-adsorption effects: FL sorption increased by only approximately 0.08–0.12 μg·g^{-1} at 0.6 mg·L^{-1} SP and approximately 0.15–0.20 μg·g^{-1} at 4.8 mg·L^{-1} SP, corresponding to relative enhancements of < 15% (Supplementary Fig. S10). This pronounced particle-size dependence mirrors trends observed in single-solute systems and reflects the higher accessibility and density of reactive surface domains on fine, oxidized PVC MPs.

From a mechanistic perspective, the observed co-adsorption behavior suggests that SP primarily occupies weak or intermediate-affinity domains on PVC surfaces, such as hydrophobic or transitional polarity regions, rather than directly displacing high-affinity sites responsible for FL binding. Partial occupation of these lower-energy domains likely reorganizes interfacial water structure and modifies local surface polarity, thereby increasing the accessibility or effectiveness of higher-energy polar microdomains on aged PVC MPs. These activated domains—associated with oxygen-containing functionalities and aging-modified C–Cl environments—favor FL sorption via F···H–O hydrogen bonding, dipole–dipole interactions, and polar interfacial stabilization. In the absence of direct spectroscopic or computational evidence, Cl-associated effects are conservatively interpreted as auxiliary interfacial contributions rather than definitive halogen bonding mechanisms. Even at elevated SP concentrations, these fluorine-specific domains remain sufficiently distinct to sustain a net enhancement of FL retention, particularly on aged 1 μm PVC MPs.

Overall, the above results consistently demonstrate that aged PVC MPs, especially fine particles, function as supplementary sorbents that increase total FL retention by approximately 18%–32% under soil-relevant conditions. Rather than suppressing FL sorption, coexisting pesticides can further amplify FL stabilization by modulating interfacial domain occupancy and accessibility. These findings provide direct quantitative evidence that PVC MPs introduce mechanistically distinct sorption pathways capable of enhancing the persistence of fluorinated pesticides in agricultural soil systems.

Conclusions and environmental implications

This study systematically addressed three core objectives, quantitatively elucidating how particle size, oxidative aging, environmental chemistry, and coexisting contaminants jointly regulate the sorption of the fluorinated nematicide FL onto PVC MPs. First, regarding particle size and aging, we demonstrate that oxidative aging fundamentally transforms PVC MPs into chemically active, high-affinity interfaces for FL. Aged 1 μm PVC consistently exhibited the strongest sorption, greatest nonlinearity, and highest desorption hysteresis. Specifically, aging increased its Langmuir maximum sorption capacity (q_0) from 291.55 to 344.25 μg·g^{-1} (≈ 18%), and Freundlich affinity (K_f) increased

https://doi.org/10.48130/ebp-0026-0011

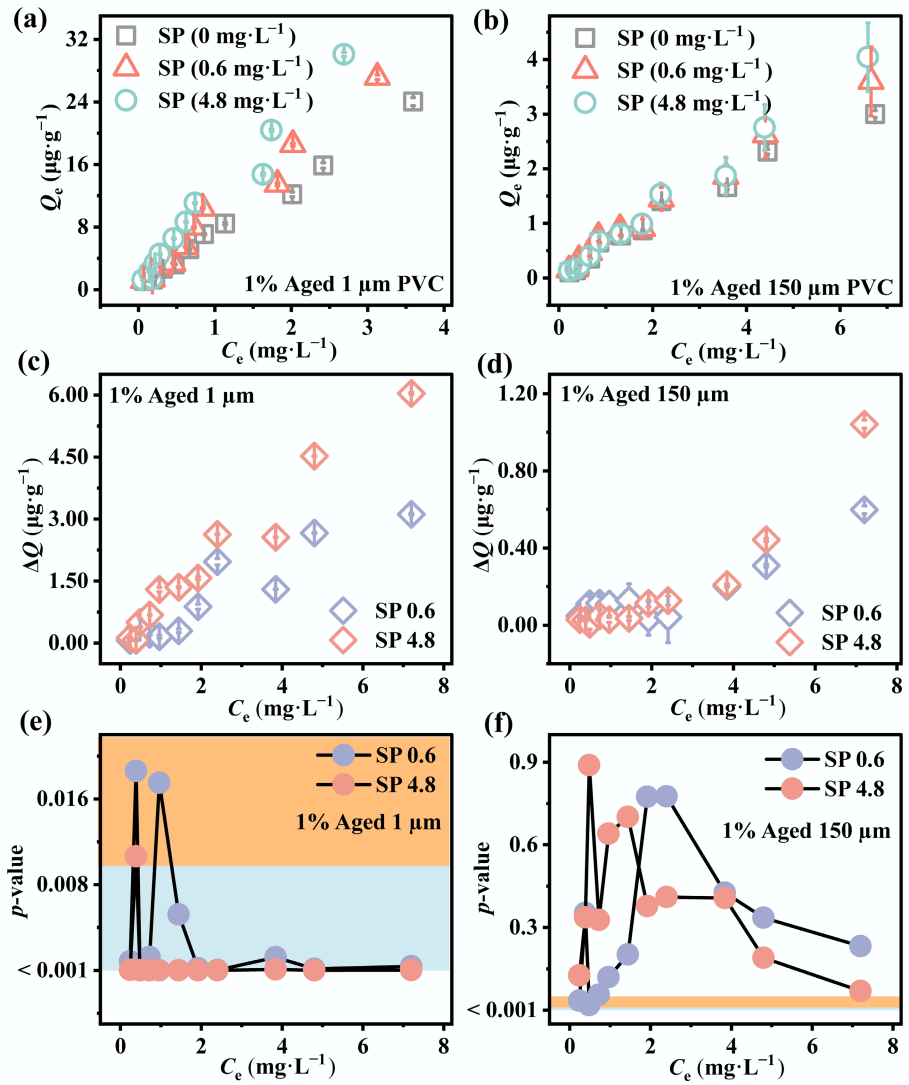


Fig. 6 Effect of coexisting SP on FL sorption in soil with 1% aged PVC MPs. FL sorption in the presence of SP at 0, 0.6, and 4.8 mg·L^{-1} for (**a**) 1 μm, and (**b**) 150 μm PVC. (**c**), (**d**) Net changes in sorption relative to the control. (**e**), (**f**) Statistical significance of these changes (Student's *t*-test).

from 43.47 to 66.35, while the nonlinearity parameter *n* decreased from 0.77 to 0.60, indicating the emergence of heterogeneous, high-energy binding domains. These changes are attributed to aging-induced increases in surface polarity, oxygen-containing functional groups, and micro-/mesoporosity, which collectively enhance F···H–O hydrogen bonding, polar interactions, and pore-assisted retention, with possible secondary contributions from C–Cl-related interfacial domains. Second, with respect to environmental chemistry, pH and dissolved ions modulated FL sorption in a manner inconsistent with classical hydrophobic partitioning. FL sorption increased monotonically with pH from 4 to 12; for aged 1 μm PVC, the equilibrium sorption capacity rose from approximately 200 to 378 μg·g^{-1}. Ion effects further highlighted specific interactions: Ca^{2+} promoted sorption (increasing Q_e by approximately 30%–35%), while Na^{+} suppressed it (by approximately 20%–40%). These results confirm that FL sorption is governed by fluorine-sensitive, surface-mediated interactions responsive to interfacial hydration and coordination chemistry. Third, in soil-relevant and multisolute systems, PVC MPs act as supplementary sorbents. Soil organic matter remained the dominant sink, yet the addition of aged 1 μm PVC produced a positive net sorption increment (Δ*Q* of approximately 0.3–0.8 μg·g^{-1}), enhancing total sorption by approximately 12%–33%. Partitioning analysis showed that aged 1 μm PVC accounted for approximately 30%–35% of total FL sorption. Notably, coexisting SP further increased FL retention on aged PVC by approximately 18%–32%, demonstrating that co-adsorption can reorganize interfacial domains to enhance stabilization.

Collectively, these findings indicate that FL sorption onto PVC MPs is governed by fluorine-sensitive interfacial interactions, which are enhanced by aging, reduced particle size, alkaline conditions, and divalent cations. These interactions primarily involve hydrogen bonding and polar stabilization, while contributions associated with modified C–Cl environments are considered secondary. Environmentally, this implies that aged PVC MPs—especially fine particles—may increase the long-term retention and persistence of fluorinated pesticides in agricultural soils, particularly under multisolute conditions. These results highlight the necessity of including MPs as active supplementary adsorbents with unique binding mechanisms in the future assessment of pesticide migration, fate, and risk evaluation.

Supplementary information

It accompanies this paper at: https://doi.org/10.48130/ebp-0026-0011.

Ethical statements

Not applicable.

Author contributions

The authors confirm their contributions to the paper as follows: Aoze Li: writing – original draft, methodology, investigation, formal analysis, conceptualization; Yiming Hou: validation, investigation; Siwei Gao: validation, investigation; Xiaoyun Li: writing – review & editing, supervision, conceptualization, funding; Shang Gao: validation, investigation; Ben Philpot: investigation; Ian Eggleston: validation, methodology; Baoshan Xing: writing – review & editing, supervision, resources, conceptualization, funding. All authors reviewed the results and approved the final version of the manuscript.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments

Not applicable.

Funding

This work was funded by the United States Department of Agriculture Hatch program (Grant No. MAS 00616), the National Natural Science Foundation of China (Grant No. 42177202), and the Fundamental Research Funds for the Central University (Grant No. GK202501007).

Declarations

Competing interests

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

Author details

[1]Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, USA; [2]Department of Environmental Science, School of Geography and Tourism, Shaanxi Normal University, Xi'an 710119, China; [3]Yulin Research Institute, School of Geography and Tourism, Shaanxi Normal University, Xi'an 710119, China

References

[1] Yang L, Yang W, Li Q, Zhao Z, Zhou H, et al. 2025. Microplastics in agricultural soils: sources, fate, and interactions with other contaminants. *Journal of Agricultural and Food Chemistry* 73:12548−12562

[2] Büks F, Kaupenjohann M. 2020. Global concentrations of microplastics in soils – a review. *Soil* 6:649−662

[3] Kedzierski M, Ciriederf-Boulant D, Palazot M, Yvin M, Bruzaud S. 2023. Continents of plastics: an estimate of the stock of microplastics in agricultural soils. *Science of The Total Environment* 880:163294

[4] Khan MA, Huang Q, Khan S, Wang Q, Huang J, et al. 2023. Abundance, spatial distribution, and characteristics of microplastics in agricultural soils and their relationship with contributing factors. *Journal of Environmental Management* 328:117006

[5] Qi R, Tang Y, Jones DL, He W, Yan C. 2023. Occurrence and characteristics of microplastics in soils from greenhouse and open-field cultivation using plastic mulch film. *Science of The Total Environment* 905:166935

[6] Li J, Zhu B, Huang B, Ma J, Lu C, et al. 2023. Vertical distribution and characteristics of soil microplastics under different land use patterns: a case study of Shouguang City, China. *Science of The Total Environment* 903:166154

[7] Jeschke P. 2024. Recent developments in fluorine-containing pesticides. *Pest Management Science* 80:3065−3087

[8] Alexandrino DAM, Almeida CMR, Mucha AP, Carvalho MF. 2022. Revisiting pesticide pollution: the case of fluorinated pesticides. *Environmental Pollution* 292:118315

[9] WHO F. 2024. *Report 2023: Pesticide residues in food*. Rome, Italy. doi: 10.4060/cc9755en

[10] Wang T, Yu C, Chu Q, Wang F, Lan T, et al. 2020. Adsorption behavior and mechanism of five pesticides on microplastics from agricultural polyethylene films. *Chemosphere* 244:125491

[11] Fan X, Zou Y, Geng N, Liu J, Hou J, et al. 2021. Investigation on the adsorption and desorption behaviors of antibiotics by degradable MPs with or without UV ageing process. *Journal of Hazardous Materials* 401:123363

[12] Li J, Huang X, Hou Z, Ding T. 2022. Sorption of diclofenac by polystyrene microplastics: kinetics, isotherms and particle size effects. *Chemosphere* 290:133311

[13] Smaili H, Ng C. 2023. Adsorption as a remediation technology for short-chain per-and polyfluoroalkyl substances (PFAS) from water – a critical review. *Environmental Science: Water Research & Technology* 9:344−362

[14] Hu B, Li Y, Jiang L, Chen X, Wang L, et al. 2020. Influence of microplastics occurrence on the adsorption of 17β-estradiol in soil. *Journal of Hazardous Materials* 400:123325

[15] Liu W, Pan T, Liu H, Jiang M, Zhang T. 2023. Adsorption behavior of imidacloprid pesticide on polar microplastics under environmental conditions: critical role of photo-aging. *Frontiers of Environmental Science & Engineering* 17:41

[16] Wang Y, Wang X, Li Y, Li J, Liu Y, et al. 2021. Effects of exposure of polyethylene microplastics to air, water and soil on their adsorption behaviors for copper and tetracycline. *Chemical Engineering Journal* 404:126412

[17] Brewer A, Dror I, Berkowitz B. 2021. The mobility of plastic nanoparticles in aqueous and soil environments: a critical review. *ACS ES&T Water* 1(1):48−57

[18] Zhao W, Chen G, Jiao J, Liu Z, Zhou Y, et al. 2025. Effects of co-existing microplastics on adsorption–desorption behavior of perfluorooctanoic acid in soil: co-sorption and mechanism insight. *Agronomy* 15:2802

[19] Du M, Pu Q, Li X, Yang H, Hao N, et al. 2023. Perfluoroalkyl and polyfluoroalkyl substances (PFAS) adsorbed on microplastics in drinking water: implications for female exposure, reproductive health risk and its mitigation strategies through in silico methods. *Journal of Cleaner Production* 391:136191

[20] Zhang Z, Liu S, Wang X, Huang S, Sun K, et al. 2023. Differences in structure and composition of soil humic substances and their binding for polycyclic aromatic hydrocarbons in different climatic zones. *Environmental Pollution* 322:121121

[21] Liu Q, Wu D, Pan Y, Shen Y, Wang X, et al. 2024. Interaction behavior, mechanisms and hazardous changes of microplastics on single and binary component pesticide in the environment and food: diethofencarb and pyrimethanil. *Journal of Hazardous Materials* 475:134809

[22] Zhao Y, Pan Z, Chen J, Lu J, Ruan HD, et al. 2025. Competitive and synergistic sorption of norfloxacin and bisphenol A onto two different microplastics. *Journal of Environmental Quality* 54:1817−1833

[23] Mo Y, Chen H, Li Y, Chen B, Wu L, et al. 2025. Co-adsorption of heavy metals and antibiotic pollutants by microplastic in aquatic

https://doi.org/10.48130/ebp-0026-0011

environments and its mechanisms: a review. *Journal of Environmental Chemical Engineering* 13(6):119436

[24] Jagani R, Patel H, Chovatiya J, Andra SS. 2025. The rise and risks of fluorinated pesticides: a call for comprehensive research to address environmental and health concerns. *Journal of Agricultural and Food Chemistry* 73:2217−2220

[25] He W, Liu S, Zhang W, Yi K, Zhang C, et al. 2023. Recent advances on microplastic aging: identification, mechanism, influence factors, and additives release. *Science of The Total Environment* 889:164035

[26] Liu P, Zhan X, Wu X, Li J, Wang H, et al. 2020. Effect of weathering on environmental behavior of microplastics: properties, sorption and potential risks. *Chemosphere* 242:125193

[27] Bhagat K, Barrios AC, Rajwade K, Kumar A, Oswald J, et al. 2022. Aging of microplastics increases their adsorption affinity towards organic contaminants. *Chemosphere* 298:134238

[28] Doussiemo DRB, Dupont A, Jafari M, Mauries S, Frenette M, et al. 2026. Different weathering strategies result in different surface properties and adsorption behavior in aged microplastics. *Environmental Science & Technology* 60(21):15218−15230

[29] Binda G, Kalčíková G, Allan IJ, Hurley R, Rødland E, et al. 2024. Microplastic aging processes: environmental relevance and analytical implications. *TrAC Trends in Analytical Chemistry* 172:117566

[30] Weber WJ Jr, Morris JC. 1963. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division* 89:31−59

[31] Wang L, Yang H, Guo M, Wang Z, Zheng X. 2023. Adsorption of antibiotics on different microplastics (MPs): behavior and mechanism. *Science of The Total Environment* 863:161022