Research article

Effect of tank-mixed adjuvant on the behavior of chlorantraniliprole and difenoconazole in soil

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A B S T R A C T

In this study, both laboratory and field studies were performed to analyze the effect of the presence of tank-mixed methylated plant oil adjuvant on the adsorption and degradation of chlorantraniliprole (CAP) and difenoconazole (DIF) in soil. Adsorption kinetics and isotherms experiments were conducted according to the equilibrium oscillation method. Fourier transform infrared spectroscopy (FT-IR) analysis, soil contact angle, and zeta potential were used to research the interaction mechanism of adsorption. Fluorescence excitation emission matrix (FEEM) measurements were conducted to characterize soil dissolved organic matter. Field experiment was conducted to investigate the degradation of CAP and DIF combined with adjuvant. DIF exhibited a significantly higher Freundlich maximum adsorption capacity than CAP, which is consistent with the higher octanol–water partition coefficient of DIF. The sorption of CAP and DIF under laboratory conditions was significantly increased with the presence of adjuvant. Soils with high humic acids have strong adsorption capacity and contribute to significant adsorption of CAP and DIF. The half-lives of CAP and DIF tested in fluvo-aquic soil under field conditions were slightly reduced by the adjuvant. Adjuvant reduced the Groundwater Ubiquity Score (GUS) indices of CAP from 1.51 to 1.31, whereas that of DIF from 0.39 to 0.25. Combination between the pesticides and soil molecules can be enhanced, thereby promoting the adsorption and degradation of CAP and DIF in soil, and further reducing their potential to leach into groundwater when 0.1% methylated plant oil adjuvant was mixed and applied.

1. Introduction

The extensive use of pesticides leads to pollution of non-target areas, such as water, soil, and the atmosphere. Therefore, the off-target deposition of pesticides on soil is a key environmental concern. Most pesticides in the surface water and all pesticides in groundwater enter via the soil [2]. The subsequent behavior of pesticides, particularly degradation and adsorption, directly influence the mobility of pesticides within soil and their transfer from soil to water, air, or food [2].

In general, pesticides adsorption is controlled by the combined effects of physicochemical properties of soils and pesticides [15]. The organic matter content is the most significant soil property affecting pesticide adsorption [27,37]. The adsorption of individual pesticides is also related to the soil clay content [12,16,37] and cation exchange capacity [16], and negatively correlated with soil pH

[34].

Another factor influencing pesticide behavior in soil is the use of adjuvants, which are divided into formulation adjuvants and tank-mixed adjuvants. As a vital part of formulation adjuvants, many authors have studied the effect of surfactants on pesticides behavior. Surfactants previously adsorbed into the soil, which typically exist at very low concentrations, can adsorb pesticides, thereby reducing pesticides mobility [30]. For example, the surfactant sodium dodecylbenzenesulfonate affects the leaching of aldicarb in soil by influencing its water solubility, adsorption and degradation [6]. The mobility of S-metolachlor increased because of the present surfactants in the formulation, which may result in increased diffusion to sediment [11]. Moreover, a previous study showed that the relative leaching difference between commercial pesticide formulations and technical pesticide materials increased with the solubility of pesticides in water, for example, 1.4 for azoystrobin while the factor of was 4.3 for the more water-soluble triadimenol [13]. However, no differences were observed in the adsorption of technical and formulated propyzamide, but leached mass of formulated propyzamide was significantly greater than that of technical propyzamide [14]. In other cases, several surfactants increased pesticide desorption, and hence, pesticide mobility [31]. The adsorption of cyanazine and atrazine was reduced in most soils with nonionic adjuvant, and compared to water, solutions containing adjuvant increased desorption of both pesticides [18].

Tank-mixed adjuvants can be divided into organic silicon, non-ionic surfactants, mineral oil, and plant oil adjuvants according to their ingredients. Compared with other adjuvants, plant oil adjuvants exhibit good biodegradability and are not restricted by pH, environmental temperature, or humidity. Tank-mixed adjuvants improve the retention, deposition, spreading, and penetration of pesticides on target crops [29], and also reduced pesticide usage and dietary exposure risk [36]. For example, organosilicone surfactants can improve the processes of water and nutrients acquisition by increasing the lettuce leaf area, reducing root dry weight and root-to-shoot ratio, and increasing the utilization efficiency of P, K, and some micronutrients [3]. However, a previous study showed that the toxicity of surfactants used as seed coating depends on the type and concentration of surfactants, thereof sodium dodecyl sulfate was the most hazardous for onion and lettuce seeds [10]. The anionic surfactant dodecyl sulfate stress significantly inhibited the root length of the wheat seedlings, and gradually reduced the protein content of shoots [4]. In the cuticular layer of plant leaf cells, surfactants may interact with lipo-proteins, weakening the cell membrane and eventually causing complete apoptosis [1]. Adjuvants will inevitably enter soil during the application process. The appropriate adjuvants can improve the environmental behavior of pesticides and remediate soil [18].

Anthranilic diamide pesticide chlorantraniliprole (CAP) has a considerable impact on the management of rice leaf roller (*Cnaphalocrocis medinalis*), Asiatic rice borer (*Chilo suppressalis Walker*), and diamondback moth (*Plutella xylostella* L.) [32]. However, CAP is highly toxic to aquatic invertebrate species. Difenoconazole (DIF) is extensively used to control fungal diseases in crops, such as rice sheath blight and Colletotrichum capsici [23], but also reduces the soil bacterial community diversity as well as exhibits negative effects on various non-target aquatic creatures, such as zebrafish and marine medaka [9,39]. In recent years, plant oil tank-mixed adjuvants have become increasingly popular. CAP and DIF are often used in combination with plant oil tank-mixed adjuvants to control pests and diseases for crops such as rice, maize, soybean, and cotton. Although CAP and DIF are used as a foliar spray, fraction of them can eventually reach agricultural soils [22,28]. Therefore, it is important to investigate the environmental fate of CAP and DIF applied in combination with adjuvants.

The purpose of this study is to evaluate the effect of the methylated plant oil adjuvant Alfaton on the behavior of two pesticides (CAP and DIF) in five typical soils via laboratory and field experiments. Specifically, 1) to examine the adsorption kinetics and isotherms of the pesticide active ingredients, formulation either when applied alone to the soils or with the adjuvant; 2) to ascertain the effect of soil types on pesticide adsorption; 3) to ascertain the effect of the adjuvant on the degradation of pesticides in fluvo-aquic soil; 4) to estimate the effect of the adjuvant on the leaching potential of pesticides in fluvo-aquic soil. The findings of the study will be useful in assessing the safe and rational usage of pesticides and tank-mixed adjuvant and the risk on the soil ecosystem.

2. Materials and methods

2.1. Soil samples

Samples from the top 0–20 cm of the soil were randomly collected from five provinces in China. The samples were air-dried, ground, and sieved (2-mm sieve) before analysis. Soils characteristics and sampling sites are listed in Table 1.

Table 1
Soils properties.

Soil	Collection site	pH	OM (%)	CEC (cmol (+) kg)	Sand (%)	Silt (%)	Clay (%)	Moisture (%)	Soil texture
Red Soil	Changsha, Hunan	5.29	0.344	16.8	54.09	27.59	18.33	2.864	Sandy loam
Paddy Soil	Shaoxing, Zhejiang	5.37	3.23	15.8	1.88	63.29	34.84	2.977	Silty clay loam
Cinnamon soil	Langfang, Hebei	5.94	1.43	14.8	36.35	41.14	22.52	2.288	loam
Black Soil	Gongzhuling, Jilin	7.52	3.34	27.6	15.37	43.79	40.85	4.072	Silty clay
Fluvo-aquic soil	Haidian, Beijing	8.48	1.88	18.9	15.48	44.96	39.57	3.226	Silty clay loam

OM: organic matter content; CEC: cation exchange capacity.

2.2. Chemicals

Analytical standards of CAP (98.3% purity) and DIF (99.3% purity) were obtained from Shanghai Pesticide Research Institute Co., Ltd. (Shanghai, P. R. China) and Beijing Tanmo Quality Inspection Technology Co., Ltd. (Beijing, P. R. China), respectively. Anhydrous calcium chloride, sodium chloride, and anhydrous magnesium sulfate, obtained from the Beijing Chemical Reagent Company (Beijing, P. R. China), were baked at 110 °C for 8 h before use. Agela Cleanert C18 sorbent (40–60 μm) was obtained from Agela Technologies (Tianjin, P. R. China). Acetonitrile (ACN, HPLC grade) was obtained from Fisher Scientific (Pittsburgh, PA, USA). Anhydrous ethanol and formic acid (98% purity) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P. R. China). Ultrapure water was obtained from the Aquapro Ultrapure Water System (Chongqing, P. R. China). CAP 200 g L^{-1} aqueous suspension concentrate (200 g L^{-1} CAP SC) (FMC Co., Ltd, PA, USA), DIF 40% aqueous suspension concentrate (40% DIF SC) (Shandong Qingdao Odis Biological Technology Co., Ltd, P. R. China), and Alfaton adjuvant (Hebei Mingshun Agricultural Technology Co., Ltd, P. R. China), of which the main component was methylated plant oil, were used for the experiments.

The standard stock solutions (1000 mg L^{-1}) of CAP and DIF were prepared in ACN and stored at a temperature of less than −18 °C. Different concentrations of working standard solutions were prepared from the standard stock solutions with ACN, as required. The physicochemical properties of CAP and DIF are listed in Table 2.

2.3. Adsorption kinetics experiments

Adsorption was evaluated for the active ingredient (AI), the SC alone, and the SC with adjuvant. Two grams of soil were placed into a 50-mL centrifuge tube. Then, 10 mL of 0.01 M CaCl$_2$ aqueous solution containing 2 mg L^{-1} pesticide was added. The samples were shaken at 25 °C for 0, 1, 2, 4, 8, 12, and 24 h. The suspension was centrifuged at a relative centrifugal force (RCF) of 3802×g for 5 min. Then, 5 mL of the suspension was filtered through a polyethersulfone filter (0.22 μm). The initial and final equilibrium pesticide concentrations in the solutions were measured by high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS).
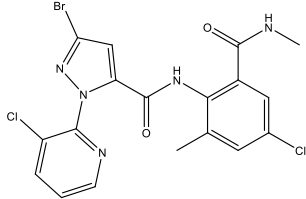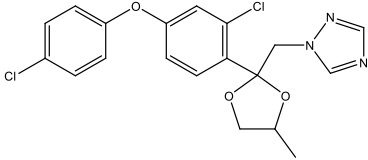
2.4. Adsorption-desorption isotherms

Adsorption was evaluated for the AI, SC alone, and SC with adjuvant for both pesticides. Soil was mixed with solutions at various pesticides concentrations (0.1, 0.2, 0.5, 1.0 and 2.0 mg L^{-1} in 0.01 M CaCl$_2$). The solubility of the pesticides in the initial water solutes (1000 mg L^{-1}) was improved by ACN (v/v 10%). Adjuvant Alfaton was added into each pesticide solution (v/v 0.1%) for the treatments with adjuvant. In triplicate, 2 g of soil was placed into a 50-mL centrifuge tube. 10 mL of pesticide solution was then added. The samples were treated as specified in Section 2.3.

An isothermal desorption test was conducted immediately following the isothermal adsorption test. Briefly, 5 mL of the centrifuge

Table 2

Pesticides' water solubility, octanol–water partition coefficient (Log K_{OW}), vapour pressure, Henry's law constant, dissociation constant (pKa), Freundlich sorption coefficient K$_f$ and K$_{fOC}$, Freundlich empirical coefficient 1/n, half-life in soil in field condition, groundwater ubiquity score (GUS), H-bond donors, H-bond acceptors and polar surface area.

	Chlorantraniliprole	Difenoconazole
CAS number	500,008-45-7	119,446-68-3
Molecular structure		
Water solubility (mg L^{-1}) at 20 °C[a]	0.88	15
Log K_{OW}[a]	2.86	4.36
Vapour pressure at 20 °C (mPa)[a]	6.3×10^{-9}	3.33×10^{-5}
Henry's Law constant at 25 °C (Pa m^3 mol^{-1})[a]	3.2×10^{-9}	9.0×10^{-7}
pKa at 25 °C[a]	10.88	1.07
K$_f$ (cm$^{3/n}$ μg$^{1-1/n}$ g^{-1})[a]	2.95	41
K$_{fOC}$ (cm$^{3/n}$ μg$^{1-1/n}$ g^{-1})[a]	301	3760
1/n[a]	0.95	0.87
Field half-life (d)[a]	204	91.8
GUS[a]	3.51	0.83
H-bond donors[b]	2	0
H-bond acceptors[b]	4	5
Polar surface area (Å^2)[b]	88.9	58.4

[a] Pesticide Properties DataBase (PPDB) web page.
[b] PubChem open chemistry database web page.

tube's supernatant was removed and agitated for 24 h with an equivalent volume of 0.01 M CaCl$_2$. The samples were then treated as specified in Section 2.3.

2.5. Interaction mechanism experiments of adsorption in soils

Two grams of soil were placed into a 50-mL centrifuge tube. Then, 10 mL of 0.01 M CaCl$_2$ aqueous solution containing 5 mg L^{-1} pesticide was added. The samples were shaken at 25 °C for 24 h. After centrifugation at an RCF of 3802×g for 5 min, the supernatants were removed. The soil samples were freeze-dried and subjected to Fourier Transform Infrared Spectroscopy (FT-IR) analysis.

2.6. Dissolved organic matter extraction and characterization

In order to explore the influence of soil properties on adsorption, the dissolved organic matter in the soil was extracted and characterized. Two grams of soil was placed into a 50-mL centrifuge tube. Deionized water (20 mL) was then added. The samples were then shaken at 25 °C for 24 h and centrifuged at an RCF of 3802×g for 5 min, then filtered through a glass fiber filter (0.22 μm) for analysis. The dissolved organic carbon content was analyzed using a TOC analyzer (Elementar, Vario TOC, Germany) with a non-purgeable organic carbon (NPOC) approach. A UV–Vis spectrophotometer (UV 1800 PC, Beijing Tianlin Hengtai Technology Co., Ltd, P. R. China) was used to characterize the dissolved organic matter (DOM) in the soil solution. With ultrapure water as a blank, a 10-mm quartz cuvette was used to perform spectral scanning in the range of 200–700 nm to determine the absorbance value in triplicate. The fluorescence excitation emission matrix (FEEM) measurements were conducted using a fluorescence spectrometer (SHIMADZU RF-6000, Japan). The spectra were recorded upon an incremental increase in the excitation wavelength from 200 to 450 nm in 5 nm steps. The emissions were detected in 1 nm steps ranging from 230 to 600 nm. The scan speed was 6000 nm min^{-1}.

2.7. Soil contact angles

To evaluate the influence of tank-mixed adjuvant on the wettability of pesticide aqueous solution on soil particles, the contact angles of the five soils, which was used to assess the wettability of porous materials, were studied through capillary rise experiments [8]. Filter paper was placed at the bottom of the tubes of the DCAT-21 interface surface tension instrument, then loaded with the same quality of soil powder, and shaken slightly until there was no obvious change in the height; the height of the powder in each tube was set to 2.5 cm to ensure the same level of powder densification. One tube was used to measure the contact angle (CA) of soil on the surface of n-hexane, and the capillary constant C was calculated by the WASHBURN method (Eq. (1)). In triplicate, another tube was used to measure the CA of soil powder on the surface of the aqueous solution of the pesticide formulation. The CA was calculated using the software SCAT32.

$$\cos \theta = \frac{m^2 \eta}{t \rho^2 \gamma C} ,$$

(1)

where θ (°) is the CA between the test liquid and the powder, m (g) is the mass of the test liquid ascending wetting, η (mPa·s) is the viscosity of the test liquid, t (s) is the wetting time, ρ (g cm^{-3}) is the wetting liquid density, γ (mN m^{-1}) is the surface tension of the test liquid, and C is the capillary constant.

2.8. Zeta potential test

In order to explore the change of the electrification of pesticide aqueous solution after adding the tank-mixed adjuvant, a Malvern laser particle sizer (Malvern Panalytical company, U.K.) was used to assess the zeta potential of the diluted solution of the pesticide formulation both with and without the adjuvant. The Zeta potential measurement vessel was thoroughly cleaned with ultrapure water and anhydrous ethanol more than ten times before being rinsed three times with the pesticide solution. The solution was then added in the proper volume and measured at 25 °C.

2.9. Field experiment

The field experiment was conducted on 8 plots (30 m^2) in 2021. CAP SC (200 g L^{-1}) and DIF SC (40%) were applied to the bare soil using a JACTO-HD400 internal pump backpack sprayer at an active constituent dose of 5 L ha^{-1} (estimated according to the initial soil deposition amount of 1 mg kg^{-1}), respectively. Both pesticides were applied without adjuvant (two plots per pesticide) as well as in a tank mixture with 0.1% (v/v) of adjuvant Alfaton (two plots per pesticide). A control treatment plot was not treated with any pesticides during the entire study period. A 30-m^2 buffer zone was established between the two plots to avoid cross-pollution. Representative soil samples were randomly collected from each plot using a soil auger to a depth of 15 cm from the surface at intervals of 0 (2 h), 1, 7, 14, 21, and 35 days in each plot after spraying. The samples were stored at a temperature of less than −18 °C and the analysis was completed within one month. Soil sample pre-treatment, HPLC-MS/MS conditions, and method validation were shown in Text S1, Text S2, and Text S3.

2.10. Fitting to models and statistical analysis

Pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models were used to fit the adsorption kinetics (Eq. (2) − Eq. (5)):

$$Q_t = Q_e \times \left(1 - e^{-k_1 t}\right) , \tag{2}$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} , \tag{3}$$

$$Q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t , \tag{4}$$

$$Q_t = k_p t^{0.5} + x_i , \tag{5}$$

where t (h) is the adsorption time; Q_t ($\mu g\ g^{-1}$) and Q_e ($\mu g\ g^{-1}$) are the sorbed amounts of pesticides in soil at time t and at equilibrium, respectively; k_1 (h^{-1}) and k_2 ($g\ \mu g^{-1}\ h^{-1}$) are the equilibrium rate constants of pseudo-first-order model and pseudo-second-order model; a ($\mu g\ g^{-1}\ h^{-1}$) and b ($g\ \mu g^{-1}$) are the Elovich constants; k_p ($g\ \mu g^{-1}\ h^{-0.5}$) is the rate constant of the intraparticle diffusion model; x_i is a number related to the thickness of the interface.

The adsorption isotherms was described by Freundlich equation (Eq. (6) − Eq. (8)):

$$Q_e = K_f C_e^{1/n} , \tag{6}$$

$$\log Q_e = \log K_f + \frac{1}{n} \times \log C_e , \tag{7}$$

$$\mathrm{HI} = (1 / n_{\mathrm{F-des}}) / (1 / n_{\mathrm{F-ads}}) , \tag{8}$$

where C_e ($\mu g\ cm^{-3}$) is the equilibrium concentration in the solution, Q_e ($\mu g\ g^{-1}$) is the amount adsorbed at equilibrium, K_f ($cm^{3/n}$ $\mu g^{1-1/n}\ g^{-1}$) is the adsorption contant, HI is the hysteresis factor, and $1/n$ $_{\mathrm{F-des}}$ and $1/n$ $_{\mathrm{F-ads}}$ represent the desorption and adsorption empirical constant, respectively.

The *OM* normalized adsorption constant K_{OM} ($cm^{3/n}\ \mu g^{1-1/n}\ g^{-1}$) was calculated by Eq. (9):

$$K_{\mathrm{OM}} = \frac{K_f}{OM} , \tag{9}$$

The free energy of adsorption was calculated according to Eq. (10):

$$\Delta G = -\mathrm{RT} \ln K_{\mathrm{OM}} , \tag{10}$$

where ΔG ($kJ\ mol^{-1}$) is the free energy of adsorption, R ($8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}$) is the molar gas constant, and T (K) is the absolute temperature.

The unit absorbance value of DOM was calculated using Eq. (11) and Eq. (12):

$$a_\lambda = \frac{2.303 A_\lambda}{r} , \tag{11}$$

$$\mathrm{SUVA}_\lambda = \frac{a_\lambda}{\mathrm{DOM}} , \tag{12}$$

where a_λ (m^{-1}) is the absorbance coefficient measured at λ nm, A_λ is the absorbance, r (m) is the path length of the optical unit, DOM ($mg\ L^{-1}$) is the dissolved organic matter content, and SUVA_λ ($L\ mg^{-1}\ m^{-1}$) is the absorbance coefficient at λ nm of the unit DOM concentration.

The residues of CAP and DIF in field soil samples were fitted to a first-order kinetics using Eq. (13):

$$C = C_0 e^{-kt} , \tag{13}$$

and pesticides half-life was calculated using Eq. (14):

$$T_{1/2} = \frac{\ln 2}{k} , \tag{14}$$

where t (d) represents the time after pesticide application, C ($mg\ kg^{-1}$) is the pesticide residue concentration at time t, C_0 ($mg\ kg^{-1}$) is the initial residue concentration, and k (d^{-1}) is the degradation rate. $T_{1/2}$ (d) represents the time required for the pesticide residue after application to drop to half of the initial residue.

The Groundwater Ubiquity Score (GUS, Eq. (15)) was used to access the groundwater leaching potential [16], and distribution

coefficient normalized by organic carbon (K_{fOC}) was calculated using Eq. (16). When GUS is higher than 2.8, pesticide is considered to have high leaching potential, and when GUS is lower than 1.8, pesticide is considered to have low leaching potential:

$$GUS = \log\left(T_{\frac{1}{2}}\right) \times \left(4 - \log K_{fOC}\right),$$ (15)

$$K_{fOC} = \frac{K_f}{OC}.$$ (16)

Here, the $T_{1/2}$ (d) value of the pesticide is calculated using Eq. (14), *OC* is the organic carbon of the soil.

The data were processed using the Microsoft Excel 2010, IBM SPSS Statistics v21 software, and Origin 2018. One-way analysis of variance (ANOVA), followed by Duncan's-test, was used to assess significant differences among different groups. Probability levels <0.05 were considered statistically significant.

3. Results and discussion

3.1. Adsorption kinetics

The adsorption kinetics of CAP and DIF onto soil exhibited a good fit to pseudo-first-order, pseudo-second-order, and Elovich model ($R^2 > 0.99$, Fig. 1 and Table S3). CAP and DIF reached their adsorption equilibrium in approximately 4 h. DIF was more thoroughly absorbed by soils than CAP. In comparison to the treatment of AI and SC, the amount of pesticide adsorbed onto the soil of the treatment SC with adjuvant was much higher. The adsorption rate of pseudo-first-order is calculated by multiplying k_1 and ($Q_e - Q_t$) [35]. Based on this, the adsorption rate in 1 h of pesticides SC with adjuvant was higher than that of AI and SC without adjuvant (except DIF on paddy soil and black soil, presumably because of the rapid adsorption achieved in a shorter time). The good fit to pseudo-second-order model indicated that surficial adsorption, mass transfer and intraparticle diffusion could occur during the adsorption process. The adsorption rate of pseudo-second-order model is calculated by multiplying k_2 and ($Q_e - Q_t$)^2 [35]. Based on this, the adsorption rate in 1 h of pesticides SC with adjuvant was higher than that of SC without adjuvant (except CAP on paddy soil, DIF on paddy soil and black soil). The good fit to Elovich model suggesting that the activation energy increased with adsorption time and the surface of the adsorbent was heterogeneous [35]. The fitting line of the intraparticle diffusion model did not pass through the origin (Table S3), indicating that intraparticle diffusion was not the solo rate controlling step in the adsorption process [21].

Based on the fitting of pseudo-first-order, pseudo-second-order, the Elovich model, and the intraparticle diffusion model, the soil pesticide adsorption process involved surficial adsorption, mass transfer, and intraparticle diffusion. Furthermore, intraparticle diffusion was not the solo rate controlling step in the adsorption process. The surface of soil was heterogeneous, and the activation energy increased with adsorption time. The adsorption rate of pesticide SC treatment with adjuvant was typically higher than that of
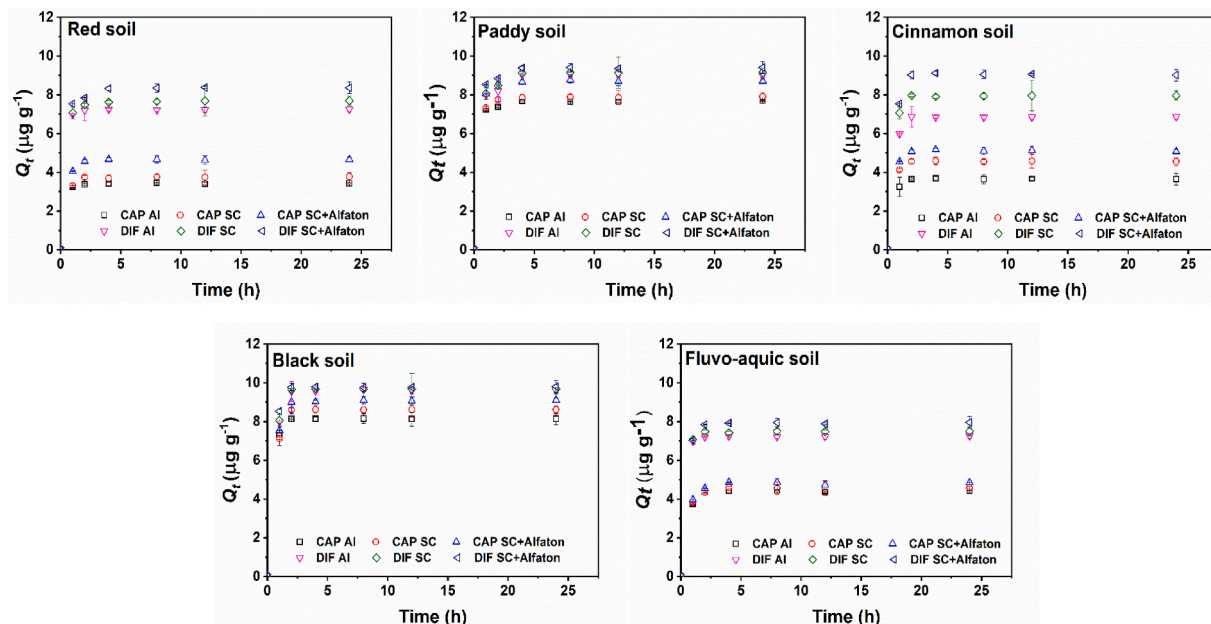

Fig. 1. Adsorption kinetics of CAP and DIF AI, SC applied alone and with the adjuvant Alfaton in five representative soils (red soil, paddy soil, cinnamon soil, black soil, and fluvo-aquic soil). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

pesticide SC and AI treatment within 1 h. Adjuvants can alter some of the physicochemical properties of the soil, thereby influencing its solid phase characteristics. The CAs of soils in the two pesticide formulations decreased after addition of the adjuvant (Table S4), indicating improved wettability [8], which may further increase adsorption capacity and adsorption rate.

3.2. Adsorption isotherms

The Freundlich adsorption and desorption isotherms observed for CAP and DIF AI and SC applied alone and with adjuvant are presented in Figs. 2 and 3. The adsorption isotherms of CAP and DIF exhibited a good fit to the Freundlich equation (Table 3; $r >$ 0.9437). The Freundlich adsorption parameters indicating that adsorption of CAP by the soil was significantly lower than that of DIF. The organic carbon−water partitioning coefficient, K_{fOC}, is commonly used to characterize the adsorption affinity of non-polar organic compounds via hydrophobic adsorption mechanisms. The K_{fOC} was 354.80–2230.87 cm$^{3/n}$ µg$^{1-1/n}$ g^{-1} and 1879.57–7301.30 cm$^{3/n}$ µg$^{1-1/n}$ g^{-1} for CAP and.

DIF, respectively, indicating that DIF was more easily adsorbed by the soil. All ΔG values in this study were negative, indicating that the adsorption was a weakly attractive exothermic spontaneous process, and that adsorption reduced as temperature rose. The hysteresis coefficients (HIs, Table 3) of CAP and DIF AI and SC applied without and with adjuvant in soils in this study were in the range of 0.68–1.20, indicating that their desorption and adsorption rates were almost equal, and that hysteresis was not significant.

According to the structure of CAP and DIF molecules (Table 2), the number of H-bond acceptors and donors, and the polar surface area of CAP are slightly higher than those of DIF. This contradicts the fact that adsorption of CAP was lower than that of DIF. Previous studies have reported that the adsorption of pesticides onto soil is positively correlated with the octanol–water partition coefficient of pesticides [19]. DIF exhibited a considerably larger octanol–water partition (log K_{OW} = 4.36) than CAP (log K_{OW} = 2.86), which supports greater DIF adsorption in soil compared to CAP, indicating that hydrophobicity plays an important role.

3.3. Influence of soil type on adsorption

The adsorption of CAP and DIF in the five soils decreased in the following order: black soil ≈ paddy soil > fluvo-aquic soil > cinnamon soil ≈ red soil (Table 3). Linear correlation analysis (Table 4) showed that the adsorption of CAP and DIF was significantly positively correlated with the soil organic matter content with P values of 0.0394 and 0.0464, respectively. In addition, the adsorption of DIF was positively correlated with the soil moisture content, cation exchange capacity (CEC), and clay content, with P values of 0.0532, 0.0620, and 0.0895, respectively.

The UV–Vis adsorption spectrum can reflect the molecular structure and the properties of DOM. The SUVA254 and SUVA280 values

Fig. 2. Adsorption isotherms of CAP and DIF AI, SC applied alone and with the adjuvant Alfaton in five representative soils. A, B, C, D, and E represent red soil, paddy soil, cinnamon soil, black soil, and fluvo-aquic soil, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
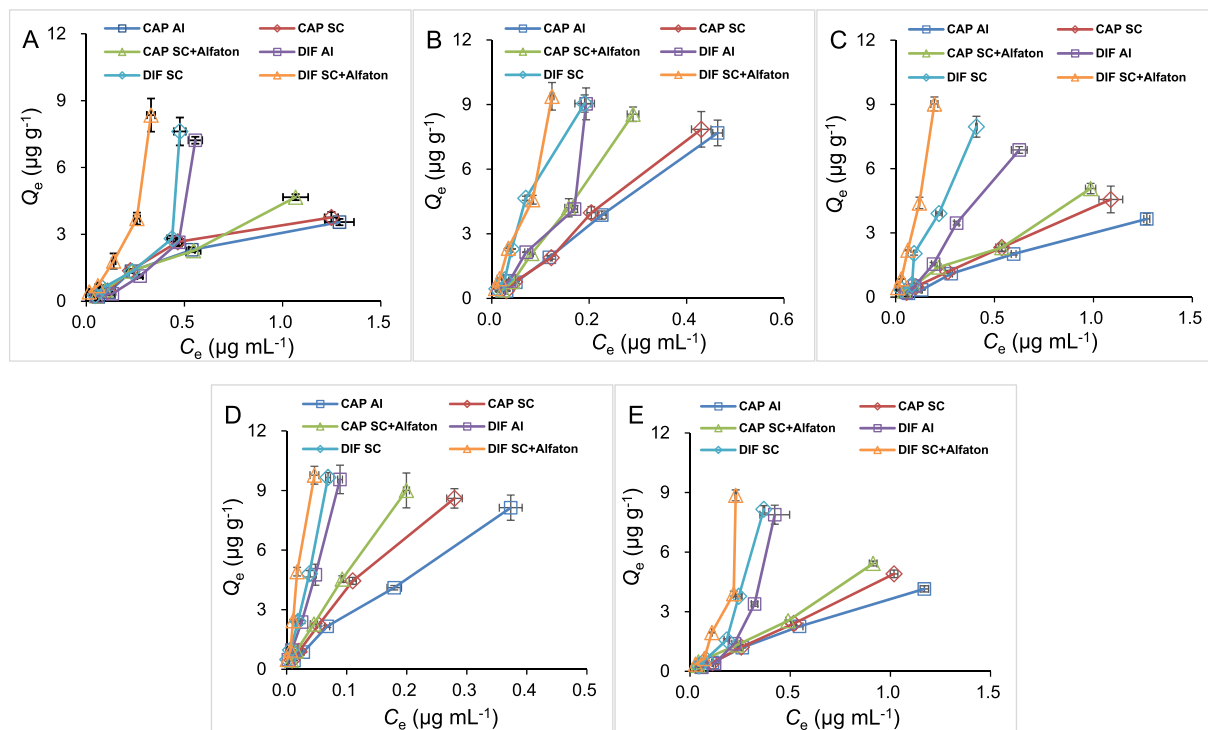
Fig. 3. Desorption isotherms of CAP and DIF AI, SC applied alone and with the adjuvant Alfaton in five representative soils. A, B, C, D, and E represent red soil, paddy soil, cinnamon soil, black soil, and fluvo-aquic soil, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
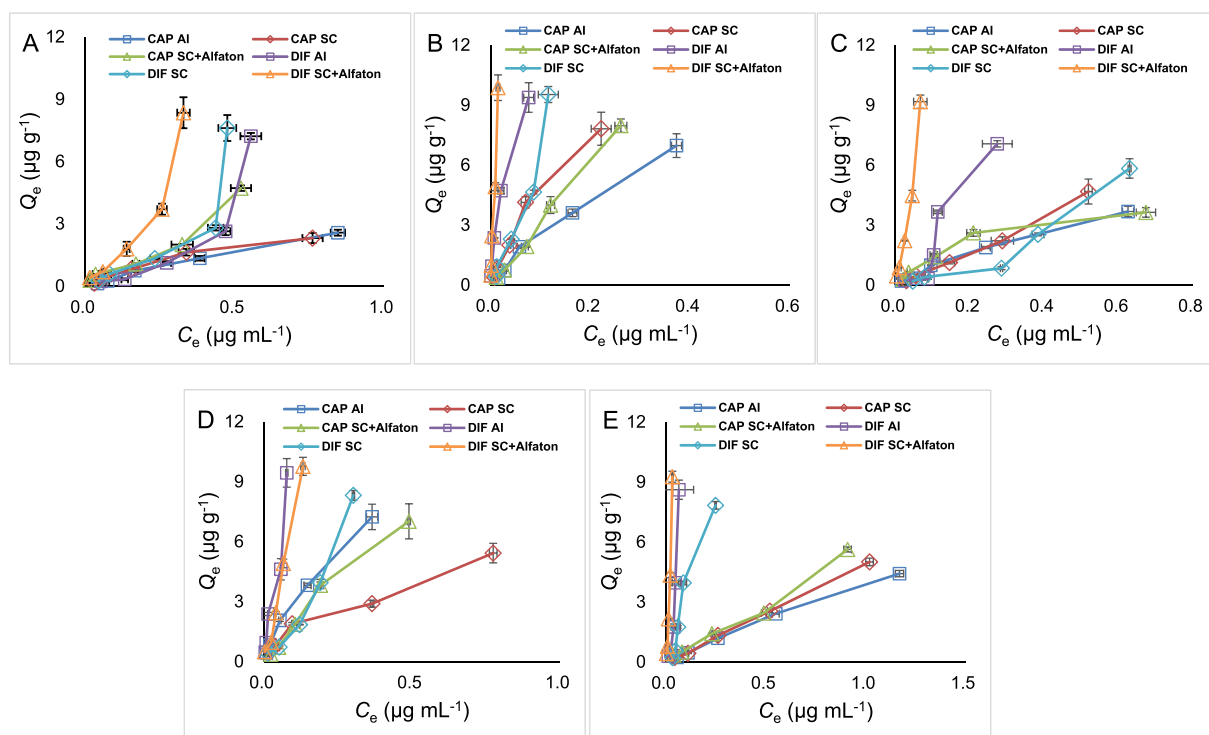
Table 3
Freundlich adsorption isotherm parameters for CAP and DIF AI, SC applied alone and with adjuvant.

Soil	Treatment	$K_{f\text{-ads}}$ (cm$^{3/n}$ µg$^{1-1/n}$ g^{-1})	$1/n_{f\text{-ads}}$	r	K_{fOC} (cm$^{3/n}$ µg$^{1-1/n}$ g^{-1})	ΔG (kJ mol^{-1})	HI
Red soil	CAP AI	3.648 ± 0.018 c	0.9688	0.9709	1823.82	−17.27	1.02
	CAP SC	3.990 ± 0.060 b	0.8790	0.9764	1995.08	−17.49	0.96
	CAP SC + Alfaton	4.462 ± 0.079 a	0.9370	0.9946	2230.87	−17.77	0.77
	DIF AI	9.106 ± 0.61 c	1.3846	0.9437	4552.91	−19.54	1.04
	DIF SC	10.825 ± 0.43 b	1.2066	0.9590	5412.41	−19.96	1.15
	DIF SC + Alfaton	14.603 ± 0.08 a	0.9286	0.9497	7301.30	−20.71	1.20
Paddy soil	CAP AI	19.568 ± 0.10 c	1.1169	0.9972	1042.00	−15.88	0.84
	CAP SC	22.101 ± 0.35 b	1.1440	0.9955	1176.90	−16.18	0.80
	CAP SC + Alfaton	39.582 ± 0.33 a	1.2162	0.9984	2107.75	−17.63	0.82
	DIF AI	38.054 ± 1.35 c	1.0889	0.9759	2026.43	−17.53	0.68
	DIF SC	64.101 ± 1.26 b	1.0945	0.9790	3413.44	−18.82	1.04
	DIF SC + Alfaton	73.100 ± 0.77 a	1.0437	0.9947	3892.65	−19.15	0.84
Cinnamon soil	CAP AI	3.254 ± 0.67 c	1.0471	0.9921	391.36	−13.45	0.80
	CAP SC	4.328 ± 0.12 b	0.9945	0.9985	520.54	−14.16	1.04
	CAP SC + Alfaton	4.794 ± 0.042 a	0.9022	0.9949	576.64	−14.41	0.81
	DIF AI	15.627 ± 0.73 c	1.4357	0.9960	1879.57	−17.34	1.04
	DIF SC	24.899 ± 1.48 b	1.2590	0.9528	2994.79	−18.50	0.96
	DIF SC + Alfaton	43.107 ± 2.64 a	1.0513	0.9914	5184.93	−19.86	0.96
Black soil	CAP AI	18.874 ± 0.36 c	0.8502	0.9980	971.96	−15.71	0.88
	CAP SC	28.157 ± 0.85 b	0.8751	0.9986	1449.99	−16.70	0.71
	CAP SC + Alfaton	39.690 ± 1.0 a	0.9180	0.9999	2043.90	−17.55	1.09
	DIF AI	68.261 ± 2.36 c	0.8706	0.9936	3515.22	−18.89	1.06
	DIF SC	74.866 ± 2.01 b	0.8302	0.9905	3855.37	−19.12	1.12
	DIF SC + Alfaton	98.690 ± 1.86 a	0.8010	0.9563	5082.22	−19.81	0.85
Fluvo-aquic soil	CAP AI	3.878 ± 0.14 c	0.9653	0.9976	354.80	−13.21	1.01
	CAP SC	4.436 ± 0.039 b	0.9373	0.9893	405.85	−13.54	1.07
	CAP SC + Alfaton	5.321 ± 0.026 a	0.9201	0.9920	486.84	−13.99	0.96
	DIF AI	28.287 ± 0.89 c	1.8511	0.9771	2587.93	−18.14	1.10
	DIF SC	32.000 ± 0.38 b	1.5586	0.9876	2927.67	−18.44	1.10
	DIF SC + Alfaton	43.924 ± 1.37 a	1.4097	0.9521	4018.56	−19.23	0.70

Table 4

Linear regression analysis for Freundlich adsorption constant of pesticides active ingredient and soil properties.

Pesticides	Linear regression parameters	Soil properties						
		pH	OM (%)	CEC (cmol (+)/kg)	Sand (%)	Silt (%)	Clay (%)	Moisture (%)
CAP	Correlation coefficient (r)	−0.0495	0.8965	0.5004	−0.7237	0.6877	0.5988	0.6126
	Significant level (P)	0.9370	0.0394	0.3906	0.1670	0.1994	0.2860	0.2720
	Intercept	11.7983	−2.5890	−5.7605	17.2686	−10.5528	−5.8304	−15.0672
	Slope	−0.2997	6.0805	0.8309	−0.3014	0.4620	0.5021	8.0740
DIF	Correlation coefficient (r)	0.4539	0.8844	0.8594	−0.6834	0.4458	0.8195	0.8732
	Significant level (P)	0.4426	0.0464	0.0620	0.2033	0.4517	0.0895	0.0532
	Intercept	−16.6880	−1.3870	−40.7895	50.8762	−3.9831	−26.2917	−64.3988
	Slope	7.4471	16.2626	3.8688	−0.7717	0.8120	1.8630	31.2004

reflect the aromaticity intensity of the DOM, where a higher value indicates more aromatic substances [20]. SUVA260 relates to the amount of hydrophobic substances in DOM [20]. Additionally, lower E250/E365 value reflects greater aromatization degree of DOM and smaller relative molecular weight [20]. The lower E465/E665 value is, the greater the polymerization of the benzene ring carbon skeleton is [33]. As shown in Fig. S1, the SUVA254, SUVA260, and SUVA280 values of the five soils decreased in the following order: black soil > cinnamon soil ≈ fluvo-aquic soil > paddy soil > red soil. For the E465/E665 values cinnamon soil showed the highest values followed by black soil, with no obvious differences among the rest of the soils. The E250/E365 values were similar and less than 3.5 for the five soils, demonstrating that the content of humic acid was higher than that of fulvic acid in the organic matter [40]. The DOM hydrophobicity of red soil was lowest, which made it simple to form complexes with pesticides via hydrogen bonds or π-π bonds in solution and accelerated the dissolution of pesticides, thereby hindering adsorption [20]. Red soil adsorbed pesticides by combining partitioning into the soil's organic matter and adsorption on the clay surface, as evidenced by the ratio of clay content to organic carbon content (RCO) of red soil being higher than 60 [17].

The FEEM analysis could reflect the fluorescence characteristics of DOM. According to Ref. [5]; the results in Fig. 4 showed the five soils had different organic compositions. None sample in the smaller molecules tyrosine aromatic protein (region I) and fulvic acid like (region III) shown a signal. The black soil and paddy soil showed stronger signals in humic acid like (region V) regions, which indicated that there were more hydrosoluble smaller-sized molecules in black and paddy soil that were water soluble. In view of above-mentioned results, the organic matters with high humic acids, that is smaller molecules, have a considerable adsorption capacity and significantly aid in the CAP and DIF adsorption processes.

3.4. Influence of adjuvant on adsorption

The adjuvant significantly increased CAP and DIF adsorption (Table 3). Many studies have reported similar results on the effects of adjuvants on pesticide adsorption in soil. The commercial formulation, for instance, exhibited a higher capacity for adsorption in the soil because penconazole in it may permeate more deeply into the less polar locations of the soil's organic matter or demonstrate co-adsorption within the oil-surfactant combination [24]. Compared to analytical-grade metalaxyl, the commercial formulation increased soil retention of metalaxyl by 30% and decreased the mobility of soluble metalaxyl in agricultural soils [26]. Moreover, adjuvants could enhanced cyprodinil and fludioxonil adsorption except at high concentrations of commercial formulations for cyprodinil [25]. In a previous study, the adjuvant negligibly increased dimethenamid-P adsorption, but significantly increased pendimethalin adsorption [15]. Dosage of surfactants may be a determinant controlling desorption and biodegradation of soil-sorbed hydrophobic organic compounds [38]. According to Ref. [7]; at temperatures below 24.5 °C, adjuvants may reduce or disrupt intermolecular interactions between pesticide molecules and soil, while the inverse was true at temperatures over 24.5 °C. This could explain our results at 25 °C.

There were C–O and C–Cl stretching vibrations of CAP and DIF in soil–pesticide complex at 1300–1000 cm^{-1} and 800–600 cm^{-1} compared to pure soil in the FT-IR spectra (Fig. S2). The intensity change of bands in the region 1300–1000 cm^{-1} suggested the occurrence of H-bonds between soil and pesticide. The intensity of the peaks of soil–CAP complex in the region 1650–1610 cm^{-1} has increased with adjuvant, which is corresponding to C=O stretching. The carbon skeleton stretching vibration in fluvo-aquic soil–pesticide complex at 1583–1378 cm^{-1} was illustrated in the FT-IR spectra. Corresponding to aromatic C=C stretching , the peak intensity in 1600–1370 cm^{-1} region of fluvo-aquic soil–DIF has increased compared to pure soil, which may due to charge–transfer bonds have formed between the soil's aromatic ring, an electron donor, and the aromatic nucleus of the DIF, an electron acceptor. According to the zeta potentials (Table S5), the adjuvant obviously reduced the negative charge of the pesticide SC aqueous solution, resulting in the electrostatic contact between the formulation and the negatively charged soil particles lower when combined with the adjuvant. In conclusion, when 0.1% adjuvant was mixed and applied, the electrostatic repulsion between pesticides and soil particles decreased, while the wettability and intermolecular force increased, consequently combination between pesticides and soil molecules can be enhanced, thereby promoting the adsorption of pesticides in soil.

3.5. Effect of adjuvant on degradation and groundwater pollution

The initial concentrations of CAP applied alone and with adjuvant in soil were 1.1 mg kg^{-1} and 1.3 mg kg^{-1} in the soil, respectively. The initial concentrations of DIF applied alone and with adjuvant in soil were 1.4 mg kg^{-1} and 1.5 mg kg^{-1}, respectively. Application
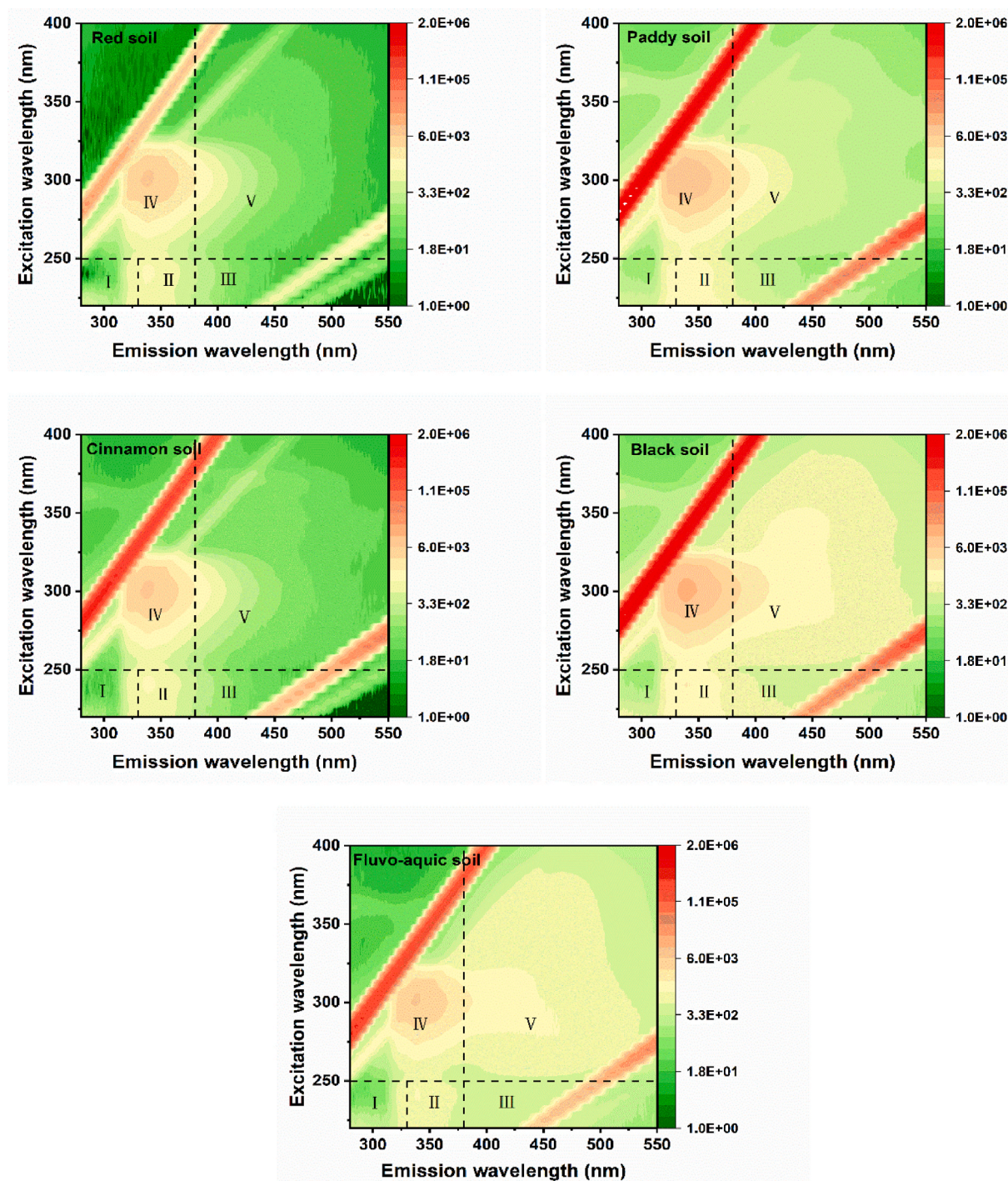
Fig. 4. Fluorescence excitation-emission matrix (FEEM) representations of dissolved organic matter (DOM) from five representative soils (red soil, paddy soil, cinnamon soil, black soil, and fluvo-aquic soil). Region I, II, III, IV, and V represent aromatic protein (smaller molecules), aromatic protein (bigger molecules), fulvic acid-like, soluble microbial by-product-like, and humic acid-like, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of the pesticides together with the adjuvant slightly increased the deposition of CAP and DIF in the soil. The degradation kinetics of CAP and DIF in fluvo-aquic soil were a good fit to the first-order kinetic model, with a correlation coefficient of $R^2 > 0.89$ (Table 5). The half-lives of CAP applied alone and with adjuvant were determined to be 12.2 days and 11.8 days, respectively, whereas those of DIF were 5.3 days and 4.3 days, respectively. The application of pesticides together with adjuvant slightly reduced the half-lives of CAP and

Table 5

First-order dynamic equation, coefficient of determination (R^2), half-life ($T_{1/2}$) and GUS of CAP and DIF SC alone and with adjuvant in fluvo-aquic soil.

Treatment	First-order dynamic equation	$T_{1/2}$ (d)	R^2	GUS
CAP-SC	$C(t) = 0.9902e^{-0.0568t}$	12.2	0.9458	1.51
CAP-SC + Alfaton	$C(t) = 0.9965e^{-0.0587t}$	11.8	0.8954	1.41
DIF-SC	$C(t) = 1.314e^{-0.1308t}$	5.3	0.9285	0.39
DIF-SC + Alfaton	$C(t) = 1.468e^{-0.1612t}$	4.3	0.9532	0.25

DIF in the soil.

Pesticide adsorption and persistence are the main determinant of the ability of pesticides to leach into groundwater from soil. The GUS indices for CAP SC alone and SC with adjuvant in fluvo-aquic soil were 1.51 and 1.31, respectively (Table 5). The GUS indices for DIF SC alone and SC with adjuvant in fluvo-aquic soil were 0.39 and 0.25, respectively. All GUS values were less than 1.8, suggesting that CAP and DIF have a low leaching potential in fluvo-aquic soil. Moreover, the adjuvant decreased the leaching capacity of CAP and DIF in fluvo-aquic soil, thereby reducing their ability to pollute groundwater.

4. Conclusion

In this study, the different behaviors of CAP and DIF in soils were documented through both laboratory and field studies. According to the laboratory study, DIF showed significantly higher values for the Freundlich adsorption parameter, K_f, than CAP, which is consistent with the higher log K_{OW} for DIF. Under laboratory conditions, CAP and DIF adsorption increased significantly in the presence of adjuvant. The soil organic matter content was the most important factor influencing pesticide adsorption, which was confirmed by the soil dissolved organic matter properties. The organic matters with high humic acids (i.e. smaller molecules) have strong adsorption capacity and contribute to significant adsorption of CAP and DIF. CAP dissipation half-lives tested in fluvo-aquic soil under field conditions (12.2 days for SC) were significantly longer than those of DIF (5.3 days for SC). The half-lives of the two pesticides were also slightly reduced by the presence of adjuvant. The half-lives of CAP SC and DIF SC applied with adjuvant were 11.8 days and 4.3 days, respectively. The GUS of CAP SC applied alone and with adjuvant was 1.51 and 1.31, respectively, whereas that of DIF SC applied alone and with adjuvant was 0.39 and 0.25, respectively. Therefore, the adjuvant reduced the GUS indices of both pesticides and therefore reduced their potential to leach into groundwater.

Declarations

Author contribution statement

Jing Jing: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Yang Zhou; Zhengyu Zhang; Lanxin Wu: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Hongyan Zhang: Conceived and designed the experiments; Wrote the paper.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no competing interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2022.e12658.

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