Sorption of penconazole applied as a commercial water–oil emulsion in soils devoted to vineyards

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ABSTRACT

The objective of this work was to assess the effect of surfactants and oils of a commercial formulation on the potential mobility of penconazole in agricultural soils that have been subjected to a high rate of application of agricultural chemicals. Soil–water partition tests on a commercial water–oil emulsion formulation of penconazole (WOEP) in 0.01 M CaCl$_2$ containing 35 mg L^{-1} penconazole, incubated for 24 h, showed a maximum retention of approximately 250–300 mg penconazole kg^{-1} soil. Approximately 70% of the total penconazole retained by the solid phase was sorbed on the soil (175–200 mg kg^{-1}). The other 30% was retained by the adjuvants present in the commercial formulation. The formulation also influenced the water–soil partition, increasing the sorption in tests on batch studies using technical-grade penconazole (TGP). Soils with high total copper and organic matter had the greatest affinity for penconazole when added as WOEP. Additionally, adsorption of penconazole followed an S-type isotherm, whose behavior was consistent with the ability of the technical-grade penconazole to form aggregates. In the case of the WOEP, the S-type behavior could be attributed to the surfactant present in the formulation, which could be adsorbed onto soil as hemimicelles, which in turn may facilitate adsorption of penconazole.

1. Introduction

Penconazole ((RS)-1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole) is a systemic pesticide used for the preventative and control of powdery mildew in vineyards and other crops. This pesticide is normally sprayed directly onto plants and is rapidly absorbed and distributed to the interior of the leaves. However, a fraction of the applied pesticide can reach the soil through drifting during application, rain washing of the pesticide off the foliage, and plant material falling to the soil [1]. Therefore, the widespread use of pesticides can lead to soil and groundwater contamination.

Sorption to soil is a key process in determining the fate of pesticides in the environment. Adsorption prevents the pesticide from polluting bodies of water but avoids its volatilization and biodegradation [2,3]. Several studies on the sorption behavior of penconazole in soils [4–8] and the correlation with soil properties, such as clay minerals [9], and the influence of pH or other chemicals (copper) in the soil [10], have been published in the past few years. However, to the best of our knowledge, all of these studies were performed using technical-grade pesticides (high purity level). Nevertheless, pesticides are not applied as pure reagents.

Commercial pesticide formulations are mixtures containing the active substances, inert material, adjuvants and other additives [11]. An adjuvant is any substance that can be added to the pesticide formulation to improve its effectiveness and make it more suitable for spray application [12]. These other substances (i.e., adjuvants and additives) present in the formulation may alter the soil–liquid partition ratio of pesticides in field conditions. For instance, the presence of higher concentrations of hydrophobic surfactants can increase the sorption of triticonazole by 50% [13]. Moreover, the influence of the commercial formulation on the pesticide behavior in vineyard soils was also observed for metalaxyl [14].

Thus, the main objective of this work was to study the sorption behavior of penconazole applied as a commercial water–oil emulsion formulation (WOEP) for a set of selected soils devoted to vineyards. The influence of the commercial formulation on the penconazole sorption process was evaluated, and the results were compared with those obtained from batch experiments with technical-grade penconazole (TGP).

2. Experimental

2.1. Soil samples

Four composite soil samples, each made up of five points from the top 20 cm, were obtained from each of four Rías Baixas

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Table 1
Soil characteristics.

Soil	pH_W	pH_{KCl}	pH_{CaCl_2}	C (%)	ECEC	Sand (%)	Silt (%)	Clay (%)	Cu_T
A	7.4	6.6	6.21	3.6	33.2	46	35	19	60
B	7.0	5.4	5.48	3.1	12.8	67	15	18	107
C	5.3	4.6	4.86	3.1	8.6	53	30	17	96
D	5.5	5.0	5.36	4.1	24.7	65	19	16	274

C, total organic carbon; ECEC, effective cation exchange capacity ($cmol_{(c)}\,kg^{-1}$); Cu_T, total Cu content ($mg\,kg^{-1}$).

vineyards in the Galician province of Pontevedra (Northwestern Spain). Once in the laboratory, the samples were thoroughly mixed and dried at room temperature, passed through a 2 mm mesh sieve, and homogenized before analysis [10]. The soils had the same sandy loam texture class, organic carbon (C) contents ranged from 3.1 to 4.1% (w/w), clay contents ranged from 16 to 19% (w/w), pH_W from 5.3 to 7.4, and pH_{KCl} from 4.6 to 6.6, as it can be seen in Table 1. The neutral pH values of soils A and B could be attributed to lime addition. The effective cation exchange capacity (ECEC) ranged from 8.6 to 33.2 $cmol_{(c)}\,kg^{-1}$. Total copper (Cu_T) contents ranged from 60 to 274 $mg\,kg^{-1}$, due to the accumulation of copper from off-target deposition of Cu-based fungicides.

2.2. Fungicides, standards and solvents

The commercial fungicide studied herein was Topas 200 EW from Syngenta Agro (O Porriño, Spain), which is a commercial oil-in-water emulsion formulation of penconazole. The main characteristics of the commercial product are summarized in Table 2. A stock standard solution of WOEP (ca. 2 g L^{-1}) was prepared in distilled water by weighing approximately 0.1 g of WOEP into a 50 mL volumetric flask and diluting to volume. The resulting penconazole concentration in this solution was 476 μg mL^{-1}. The stock suspension of WOEP was kept homogeneous by vigorous vortex stirring. Intermediate solutions were prepared in 0.01 M calcium chloride (pH 6.2).

Technical-grade penconazole was obtained from Riedel-de Haën (Seelze-Hannover, Germany), with a purity higher than 90%. A stock standard solution (ca. 1 g L^{-1}) of fungicide was prepared in methanol by weighing approximately 0.025 g of the analyte into a 25 mL volumetric flask and diluting to volume. All standard solutions were stored in the dark at 4 °C and were stable for 6 months.

The reagents used in this work were calcium chloride for residue analysis and acetonitrile, methanol and water for instrumental analysis. All of these reagents were obtained from Panreac (Barcelona, Spain).

2.3. Analytical methods

High-performance liquid chromatography (HPLC) analyses were carried out on a Thermo HPLC system equipped with a SCM1000 vacuum membrane degasser, a P4000 binary pump, an AS1000 autosampler, a column heater from Jones chromatography (Model 7981) and a microUVIS 20 detector linked to a PC computer running the ChromCard (version 2.51) software program (Termo-Quest, Rodano, Italy).

Separations were performed with a Luna C18 (150 × 4.6 mm i.d., 5.0 μm particle size) analytical column obtained from Phenomenex (Madrid, Spain) and a guard column (40.0 × 3.0 mm i.d., 5.0 μm particle size) containing the same packing material. The temperature of the HPLC column was kept constant at 40 °C. The mobile phase was acetonitrile (A) and water (B) with the following gradient: 70% of A changed to 95% of A over 7 min, held for 1 min and finally changed to 70% of A in 0.1 min, giving an analysis time of 18 min after taking into account the equilibration time. The injection volume was set

to 50 μL at a HPLC flow rate of 1.0 mL min^{-1}. Penconazole detection was carried out at 200 nm.

Prior to HPLC injection, 2 mL of the sample was filtered. Different 0.45 μm filters were assayed: polyester filters (PET) from Machery-Nagel (Hamburg, Germany), nylon filters from Afora (Barcelona, Spain), cellulose filters from Nalgene (Rochester, USA) and glass microfiber filters MFV3 from Filter-Lab (Barcelona, Spain). A syringe filter holder from SartoriusStedim (Goettingen, Germany) was used when necessary.

2.4. Water-WOEP partition

To assess the partition of penconazole between the aqueous and the emulsion phases of the WOEP formulation, a set of batch experiments was conducted in quadruplicate ($n = 4$). In each assay, a known amount of WOEP (25, 50, 100, 125, 150 and 175 mg L^{-1}; corresponding to penconazole concentrations ranging from 5 to 35 mg L^{-1}) was suspended in 10 mL of 0.01 M $CaCl_2$ solution. These suspensions were shaken in a Problot hybridization oven from Labnet (Rochester, USA) at 200 rpm for 24 h at 25 ± 1 °C, after which they were centrifuged in a Mixtasel centrifuge from JPSelecta (Barcelona, Spain) for 30 min at 300 × g, obtaining a clear separation between the supernatant (water) and sediment (WOEP). Afterwards, the pH of the supernatant was measured using a pH-meter from Crison Instruments (Barcelona, Spain), and the penconazole concentration in the liquid phase was determined by HPLC. Data for the penconazole concentration in the aqueous phase in the WOEP/0.01 M $CaCl_2$ mixtures were used as a control in calculations of the batch sorption equilibrium with soil.

2.5. Kinetic experiments

Kinetic experiments were performed to assess the time course of the phase partition and to determine the incubation time for the batch experiments. Phase partition tests were performed by sampling aliquots of a suspension of WOEP in 0.01 M $CaCl_2$ (containing 20 mg L^{-1} of penconazole) with 10 g of soil at 25 ± 1 °C. In addition, kinetic tests with a stirred suspension of TGP (20 mg L^{-1}) were also performed. In both cases, control samples were prepared

Table 2
Characteristics of the commercial product WOEP.

	Topas 200 EW
Commercial brand	Syngenta Agro, S.A.
Composition	Penconazole (20%, w/w) Naphthalenesulfonate, condensate formaldehyde, as sodium salt (0–5%, w/w) Petroleum solvent naphtha (10–15%, w/w)
CAS number	Penconazole: 66246-88-6 Naphthalenesulfonate, condensate formaldehyde, as sodium salt: 9008-63-3 Petroleum solvent naphtha: 64742-94-5
Formulation	Oil in water emulsion (EW)
Physical characteristics	Clear liquid, white to beige
Density of the formula	1.01–1.05 g/cm³
Solubility of the formula	Miscible in water

without soil (suspensions of fungicide/0.01 M CaCl$_2$). Suspension aliquots were sampled at different times (1, 4, 8 and 30 min, and 2, 8, 24, 48, 72 and 96 h) and immediately centrifuged for 30 min at $300 \times g$ to measure the concentration of penconazole in the liquid phase. These experiments were done in duplicate ($n = 2$). Stirring using a polytetrafluoroethylene (PTFE)-coated magnetic stir bar at 200 rpm was appropriate for short incubation times (less than 2 h), but experiments using orbital shaking were also conducted for longer incubation times for comparison with the batch tests.

2.6. Fungicide soil batch experiments

To assess the soil–water partitioning of penconazole at a range of concentrations, two sets of batch experiments were performed: one using TGP and the other using the WOEP formulation (containing 20%, w/w of penconazole). In each assay, 1 g of soil was suspended in 10 mL of the fungicide/0.01 M CaCl$_2$ solution, and the suspension was mixed on an orbital shaker at 200 rpm for 24 h at $25 \pm 1\,^{\circ}$C, after which it was centrifuged for 30 min at $300 \times g$. The supernatant obtained was filtered and analyzed to determine the penconazole concentration. In addition, the pH of the supernatant was also determined. All experiments were performed in triplicate ($n = 3$), and in both cases, control tests (without soil) were prepared. The maximum penconazole concentration in the sorption experiments was 35 mg L^{-1} (corresponding to 175 mg L^{-1} of WOEP), below its solubility limit in water (73 mg L^{-1} at 25 $^{\circ}$C [15]) and in agreement with the recommended application dosage of WOEP (150–250 mg L^{-1}, corresponding with a penconazole concentration of 30–50 mg L^{-1}). This is the range of concentrations expected to reach the soil surface by either spray drift or canopy drip.

For the first set of experiments, aqueous solutions of TGP (5, 10, 20, 25, 30 and 35 mg L^{-1}) were made up by adding the appropriate volume of the penconazole stock solution (1 g L^{-1} in methanol) to 0.01 M CaCl$_2$. For the second set of experiments, aqueous suspensions of the WOEP formulation (25, 50, 100, 125, 150 and 175 mg L^{-1}; corresponding to penconazole concentrations ranging from 5 to 35 mg L^{-1}) were made by adding the appropriate volume of the stock suspension of WOEP (2 g L^{-1} in distilled water) to 0.01 M CaCl$_2$.

3. Results and discussion

3.1. HPLC determination of penconazole

Penconazole determination was carried out with a HPLC-UV instrument operating at 200 nm, revealing a chromatographic peak with a retention time of 4 min. Before injecting in the HPLC, samples were filtered to remove any trace of particles present in the sample after centrifugation. To improve the recovery of penconazole in this step, different 0.45 μm filters (PET, nylon, cellulose and glass microfiber filters) were assayed. For this experiment, a known volume of TGP solution (20 μg mL^{-1}) in 0.01 M CaCl$_2$ was filtered. Afterwards, the penconazole concentration was determined by HPLC and compared with the concentration obtained without filtering. These experiments were performed in triplicate ($n = 3$). The results suggested that quantitative recoveries could only be achieved with the glass microfiber filters (96 $\pm$ 2%). The other filters showed low recoveries, and their efficiency decreased in the following order: PET (60 $\pm$ 2%) > cellulose (47 $\pm$ 7%) $\gg$ nylon (0%). In addition, the efficiency of the glass microfiber filters was also assayed with the WOEP formulation, resulting in a penconazole recovery of 96 $\pm$ 3%.
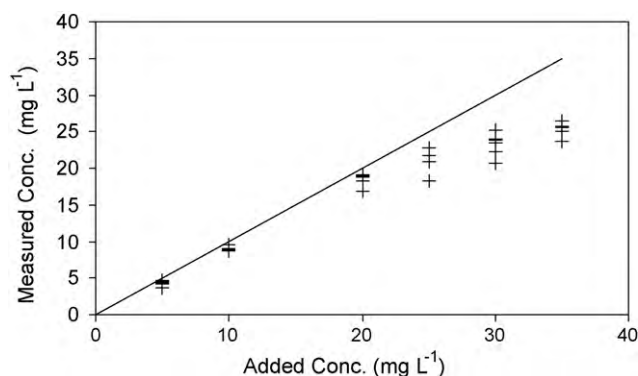

Fig. 1. Relationship between observed and calculated penconazole concentrations in solutions using the WOEP formulation. The line shows the 1:1 ratio.

Detection and quantification limits (LODs and LOQs) of the method were evaluated based on the noise obtained with the analysis of soil/0.01 M CaCl$_2$ suspensions without fungicides ($n = 7$) and were defined as the concentration of the analyte that produced a signal-to-noise ratio of 3 and 10 on average, respectively. The obtained values were 0.3 and 0.6 μg mL^{-1} for the LOD and the LOQ, respectively.

3.2. WOEP-water suspensions

Due to the variety of constituents of the commercial formulations, the interaction of penconazole with the non-soluble adjuvants of the WOEP formulation should be considered before studies with soil are carried out. As is shown in Fig. 1, the measured concentrations of penconazole in WOEP solutions were lower than those expected from the dilution. The deviation for the TGP at the high range of concentrations added was lower than that for the WOEP formulation (data not shown). This behavior demonstrated that the influence of the other ingredients of the WOEP formulation decreased the quantification in the aqueous phase. Similar result has been reported for the fungicide metalaxyl in Ridomil Gold Plus-water suspensions [14].

3.3. Kinetics

For the kinetic experiments, WOEP/0.01 M CaCl$_2$/soil suspensions were stirred using a PTFE-coated stir bar at $25 \pm 1\,^{\circ}$C. In addition, experiments with control samples (WOEP/0.01 M CaCl$_2$) were conducted. As it can be seen in Fig. 2, the kinetic behavior of penconazole was similar for the four soils studied. The
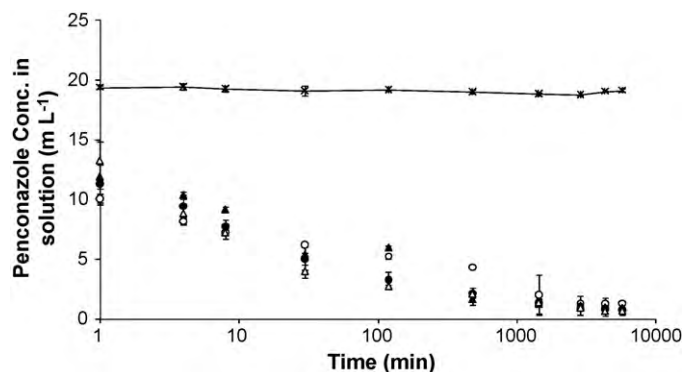

Fig. 2. Time course profile of the penconazole concentration in solution when applied as WOEP. The line denotes the control sample and symbols denote incubation with soil A (○), soil B (▲), soil C (●) and soil D (△).
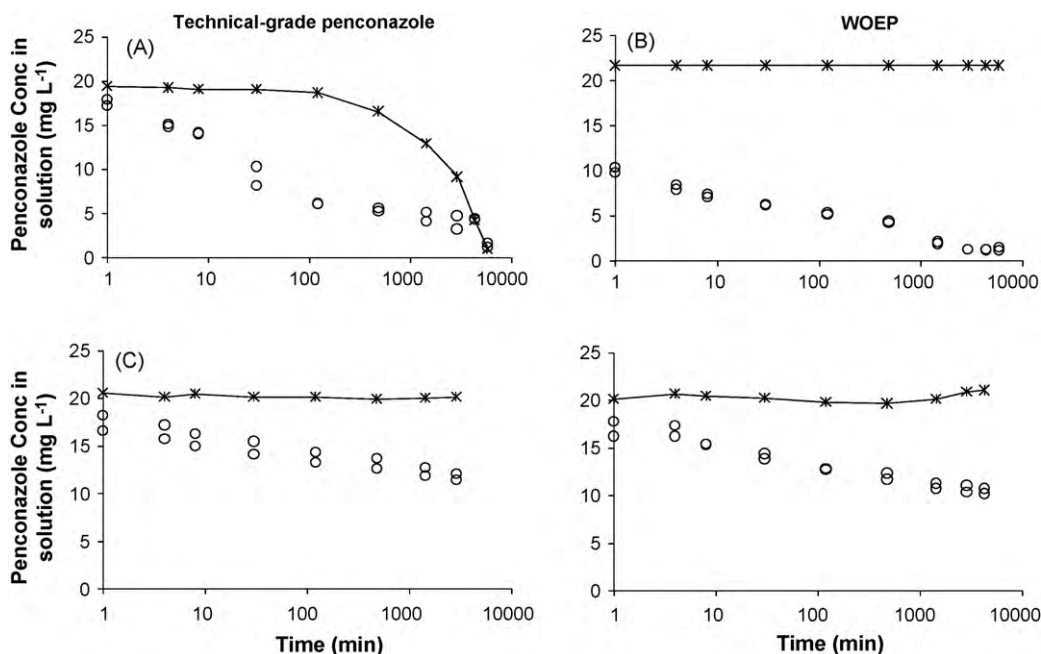
Fig. 3. Influence of shaking in the time course profile of the penconazole concentration in fungicide/0.01 M CaCl$_2$/soil A suspensions. Penconazole was applied as TGP or WOEP formulations, and suspensions were mixed with vortex stirring (A and B) or with orbital shaking (C and D). The line denotes the control sample.

dissolved penconazole concentration decay was compared to the control suspension in which decay was negligible. The decay rate decreased with time in all soils and was negligible from 48 to 96 h of incubation.

For comparative purposes, time course experiments with TGP and soil A were performed (Fig. 3a). Penconazole concentrations in these solutions decreased with time as well. In this case, however, the concentration was not at equilibrium between 48 and 96 h. In addition, it is important to note that the decay of the penconazole concentration in solution was observed even in the control suspensions, especially after 2 h of stirring (Fig. 3a). This behavior was related to the formation of flakes that became visible to the naked eye after 48 h of stirring (Figure I of the supplementary material). Microscope photographs showed that the flakes were fragments of a structure that grew as thin films on the surface of the PTFE coating the magnetic stir bar. The flakes had a moderate breaking strength and did not dissolve in methanol. These tests indicated that the technical-grade penconazole could form clusters or even polymerize on the interface of the PTFE and water. The radial structure of these flakes suggested that aggregation had its origin in isolated sites on the surface of the PTFE. In any case, the experiments with TGP/0.01 M CaCl$_2$ showed that TGP could form aggregates on a solid–liquid interface. This behavior has not been reported yet.

When the kinetic experiments with TGP were performed with orbital agitation instead of using a PTFE-coated magnetic stir bar, the profile of the curves changed drastically (Fig. 3a and c). On the one hand, when orbital shaking was used, the dissolved penconazole concentration in the control suspensions was stable throughout the analysis time. On the other hand, a lower decay of the penconazole in the fungicide/soil suspensions was observed with orbital shaking as compared to when using the PTFE-coated magnetic stir bar (decays of 32 and 77%, respectively, after 24 h of stirring). Therefore, in order to compare both formulations, time course experiments with the WOEP formulation were repeated using the orbital shaker. As it can be seen in Fig. 3d, no decay occurred in control suspensions when orbital shaking was used throughout the experiment. It was important to note that with

orbital agitation, the time course profiles obtained for the TGP and the WOEP formulations were virtually identical (Fig. 3c and d).

3.4. Fungicide soil batch experiments

Penconazole partition between the soil and the aqueous phase suspension was evaluated using TGP and WOEP. The incubation time was assumed to be 24 h using an orbital shaker. The aqueous phase was analyzed as described in Section 2.6. These experiments demonstrated that sorption of penconazole to the soil was influenced by the pH of the suspension [10]. Therefore, the shift in the pH of the suspensions induced by the fungicides was analyzed. The addition of fungicides to the control (0.01 M CaCl$_2$) increased the pH slightly after the addition of 5 mg L^{-1} penconazole of either TGP or WOEP formulations (Fig. 4). In the same way, for soils A and B the addition of 5 mg L^{-1} of penconazole, either as a TGP or WOEP formulation, promoted a pH increase by 1 unit, after which the pH was kept constant with increasing amounts of penconazole. However, when the WOEP was used, the pH increased between 1 and 1.5 units in soils C and D. In contrast, when the TGP was used, it was observed that for soil C, the pH of the suspension increased more slowly with the amount of fungicide added, achieving a final pH similar to the one obtained in the control suspension at a penconazole concentration of 35 mg L^{-1}. In the case of soil D, the pH of the suspension decreased drastically with the smaller amount of TGP added and then increased with the amount of fungicide added until it reached the initial pH. This behavior highlighted the greater buffer effect of the WOEP, as was shown in the cases of the acidic soils (soils C and D).

The penconazole concentration in the solid phase was calculated as follows:

$$C_{\text{solid}} = \frac{(C_{\text{total}} - C_{\text{liquid}}) \times V}{m} \tag{1}$$

where C_{solid} (mg kg^{-1}) was the penconazole concentration in the solid phase, C_{total} (mg L^{-1}) the estimated penconazole concentration added to the suspension, C_{liquid} (mg L^{-1}) the measured concentration in the liquid phase after incubation (24 h), V the
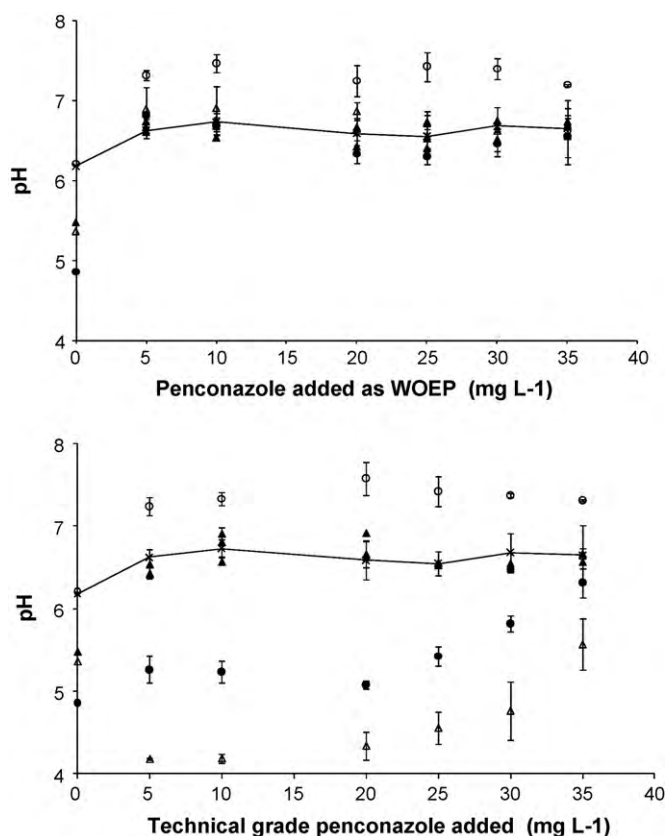
Fig. 4. pH changes in the fungicide/0.01 M CaCl$_2$/soil suspensions induced by the addition of increasing amounts of WOEP and TGP after 24 h of incubation. Symbols denote incubation with soil A (○), soil B (▲), soil C (●) and soil D (△). The line shows the control sample.

volume of the liquid phase (L), and m the mass of soil in the suspension (kg). The partition data of penconazole between the solid and the aqueous phase are shown in Fig. 5. Experimental data points showed quasi-linear to non-linear (Freundlich-type) distributions. In general, the average slope of the points was greater when using the commercial formulation than when using the TGP. Thus, higher concentration data for penconazole in solids were obtained for the WOEP formulation (250–300 mg kg^{-1}). This behavior was consistent with the decrease of the measured concentration in solution observed in control experiments, as described above (Fig. 1), suggesting that the solid adjuvants present in the commercial formulation, together with soil, contributed to increase the total penconazole concentration in the solid. A similar behavior was also observed in a previous study of the sorption of the fungicide metalaxyl by comparing the technical-grade pesticide with a commercial formulation [14]. The distribution of points in Fig. 5 for soils B and C with the WOEP formulation did not pass near the intersection of the axes. This observation could be attributed to the fact that the interaction of each soil with WOEP was different. With small additions of WOEP, the affinity for adsorption of penconazole by soils B and C was smaller than for soils A and D. This phenomenon was not detected in the case of technical-grade penconazole.

The actual sorption to soil was calculated assuming that the concentrations measured in the aqueous phase of the control test samples could be used to distinguish the penconazole sorbed to soil in the non-aqueous phase. As stated above, a fraction of the penconazole added to the suspension was retained in the non-aqueous phases of the suspension formulation and not in the soil (Fig. 1).

Sorbed concentration was calculated by

$$C_{\text{sorbed}} = \frac{(C_{\text{control}} - C_{\text{liquid}}) \times V}{m} \quad (2)$$

where C_{control} was the penconazole concentration in the solution measured in fungicide/0.01 M CaCl$_2$ suspensions without soil. It should be noted that this was a simplification that did not consider the interaction of the soil with the adjuvants and their impact on the partitioning of penconazole between phases. Sorption isotherms calculated using this equation are shown in Fig. 6. As it can be seen, sorbed concentration rose quickly, and the curves tended to plateau at high concentrations, indicating that the maximum capacity of adsorption had been reached. Penconazole adsorptions between 175 and 200 mg kg^{-1} were obtained for the target soils at the highest WOEP concentration assayed. Thus, it could be concluded that only 70% of the total penconazole retained by the solid phase was sorbed by soil. Adsorption of TGP onto soil A showed that the isotherm rose to 62 mg kg^{-1} and then descended at 30 mg kg^{-1}, which was followed by an increase to a plateau at 141 mg kg^{-1}. Note that these features of this isotherm were confirmed in triplicate experiments (Fig. 6). Furthermore, the isotherms appeared to be displaced from the origin ($x = 0$, $y = 0$), which was more pronounced in the case of WOEP than with TGP. This behavior is typical of the S-type isotherm according to the classification proposed by Giles and co-workers [16]. As they defined, the S-type isotherm indicates a tendency for adsorbed molecules to associate rather than to remain as isolated units. As stated by Giles and coworkers, the S-type curve usually appears when three conditions are fulfilled: (i) the solute molecule is monofunctional; (ii) it has moderate intermolecular attraction, causing it to pack vertically in a regular array in the adsorbed layer; and (iii) there is a strong competition for substrate sites from molecules of the solvent or of another adsorbed species. Based on these criteria, the sorption data were analyzed under the assumption of the S-type isotherm. For nonionic pesticides, such as penconazole, neither electrostatic nor strong interactions between the pesticide and the soil were present. However, the surfactant sodium naphthalene sulfonate can form hemimicelles. The role of this surfactant is to enhance the penetration of pesticides across polar–hydrophobic interfaces. In commercial formulations, adsorption of mixtures including a surfactant is cooperative. In cooperative adsorption, the surfactant can assist the pesticide to adsorb on the surface [17].

In this study, the WOEP's adjuvants may have influenced the S-type behavior. In general, the adsorption of nonionic surfactants from aqueous solution onto polar sorbents exhibits an S-type curve. This observation was described by other authors for surfactant sorption on polar surfaces where the adsorbate packed in arrays to form hemimicelles [18]. Thus, the adsorbed concentration increased dramatically as hemimicelles or clusters of molecules form on the adsorbent through association between adsorbed molecules on the surface. As the concentration increased further, the adsorption reaches the second plateau. When the affinity of the sorbent to the soil surface was low, the first plateau was absent, causing the "shift" effect observed in Fig. 6 for soils B, C and D. However, soil A with TGP/0.01 M CaCl$_2$ exhibited bimodal behavior, which suggested that the affinity of penconazole to soil A at the first stage of adsorption was high enough to show two plateaus. The disappearance of the first plateau in the isotherms made with soil A/WOEP/0.01 M CaCl$_2$ supports the hypothesis that the presence of adjuvants decreases the adsorption of isolated molecules.

Sorption isotherms were modeled based on the mass–action model for hemimicellization on a sorbent surface, as proposed by Gu and Zhu [18] to describe the behavior of an S-type isotherm. The equilibrium for aggregation of n molecules of adsorbate on a surface site (S) to form a hemimicelle, where n is the average aggregation
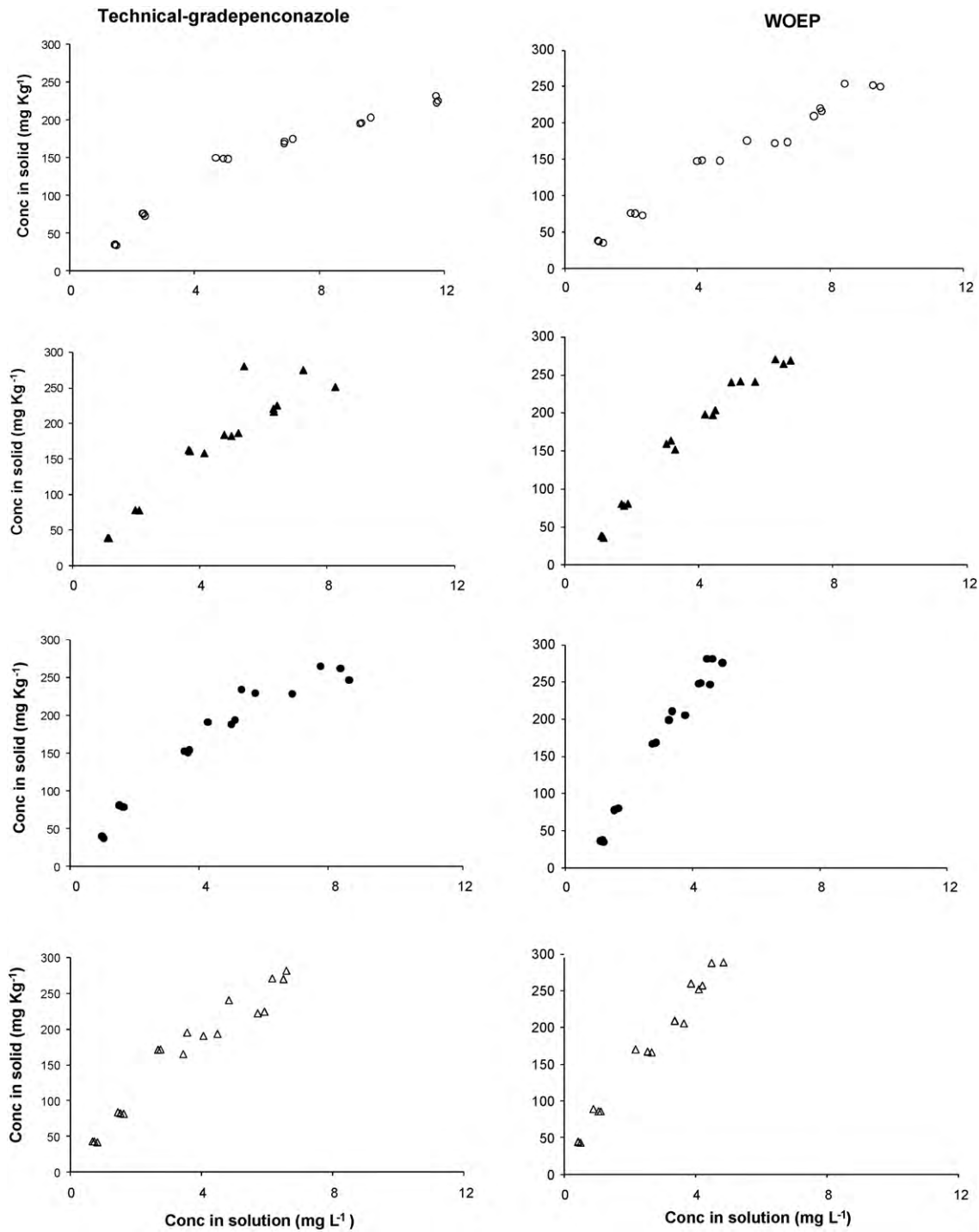
Fig. 5. Partition of penconazole, applied as the technical-grade fungicide or the WOEP formulation, between the solid and the liquid phases. The solid concentration is the difference between the penconazole concentration added to the soil (C_{total}) and the penconazole concentration measured in the solution at equilibrium (C_{liquid}). Symbols denote incubation with soil A (○), soil B (▲), soil C (●) and soil D (△).

number of the hemimicelle, can be described by

$$S + n \text{ monomer} \leftrightarrow \text{hemimicelle} \tag{3}$$

and

$$K = \frac{a_{hm}}{a_s \times a^n} \tag{4}$$

where a is the activity of the adsorbate in solution if the concentration of adsorbate is below the critical micelle concentration

(i.e., $c < $ c.m.c.), a_{hm} and a_S are the activities of hemimicelles and surface sites, respectively, and K is the equilibrium constant (for diluted solutions a–c). Approximately, $a_{hm} = S/n$ and $a_S = (S_{max} - S)/n$, where S is the concentration of adsorbate at c and S_{max} is the concentration adsorbed in the limiting adsorption. Thus, Eq. (4) for dilute solutions becomes

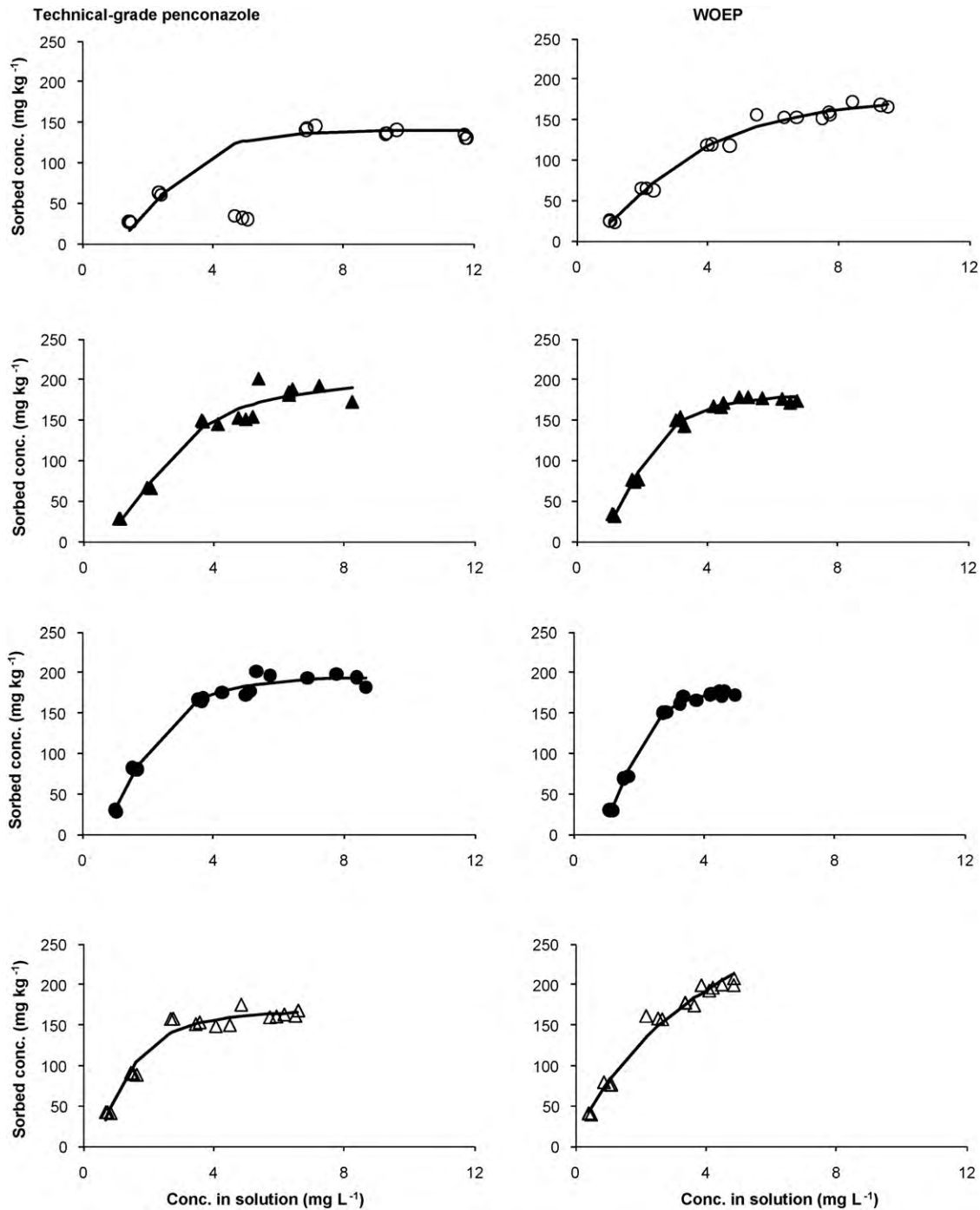$$K = \frac{S}{(S_{max} - S) \times c^n} \tag{5}$$

Fig. 6. Adsorption of penconazole, applied as the technical-grade fungicide or the WOEP formulation, between the soil and the liquid phase. The sorbed concentration is the difference between the penconazole concentration measured in the control test samples ($C_{control}$) and the penconazole concentration measured in the solution at equilibrium (C_{liquid}). Symbols denote incubation with soil A ($\bigcirc$), soil B ($\blacktriangle$), soil C ($\bullet$) and soil D ($\triangle$). Lines show the best fit to the Eq. (6) isotherm.

and Eq. (5) can be rewritten as

$$S = \frac{S_{max} \times K \times c^n}{1 + K \times c^n} \tag{6}$$

This S-type adsorption isotherm equation then allows the calculation of the aggregation number n, the equilibrium constant K and the maximum capacity of adsorption. From this equation, if hemimicellization occurs, then n should be >1; however, if multisite adsorption occurs (i.e., each adsorbed molecule occupies more than one site), then $1 > n > 0$.

The parameters of Eq. (6) were best fit by least squares minimization according to the excel-spreadsheet method described by Bolster and Hornberger [19]. The Akaike's information criterion was used to compare the best fitting results of the three-parameter S-type isotherm in relation with the two-parameter Langmuir or Freundlich isotherms. Fitting results (Table 3) showed that Eq. (6) provided a good description of the experimental data without overfitting. The fitted parameters of the model isotherms were observed to be statistically affected by the type of formulation. There were also significant differences between the soils, indicating that the intrinsic variation of soil properties influences the adsorp-

Table 3
Fitting parameters of S-type adsorption model equation [6] to the experimental adsorption isotherms.

Soil		$K \pm SD$ (L kg^{-1})	$S_{max} \pm SD$ (mg kg^{-1})	$n \pm SD$	E
A	WOEP	0.128 ± 0.016	191.2 ± 10.4	1.81 ± 0.18	0.986
	TGP	0.037 ± 0.110	141.3 ± 14.84	3.40 ± 2.91	0.702
B	WOEP	0.133 ± 0.015	183.6 ± 3.49	2.97 ± 0.21	0.992
	TGP	0.102 ± 0.025	201.8 ± 13.1	2.39 ± 0.36	0.966
C	WOEP	0.113 ± 0.009	179.9 ± 2.29	3.72 ± 0.18	0.996
	TGP	0.185 ± 0.022	196.7 ± 4.46	2.68 ± 0.24	0.988
D	WOEP	0.187 ± 0.117	506.5 ± 265	0.85 ± 0.16	0.976
	TGP	0.540 ± 0.07	171.0 ± 6.19	2.15 ± 0.29	0.962

tion parameters. With the exception of the data corresponding to soil A with TGP that showed an isotherm profile with two plateaus, equilibrium constants were in the range of 0.10–0.54 L kg^{-1} and were influenced by both the type of formulation and the type of soil. From these calculations, the maximum values of K corresponded to soil D. Additionally, the maximum capacity of adsorption (S_{max}) varied from 171 to 506 mg kg^{-1} and the maximum S_{max} was found for soil D with WOEP, while the minimum corresponded to the same soil with TGP.

Fitted values of the aggregation number n suggested that the adsorption of penconazole onto soil behaved mostly like the clustering of sorbed monomers of penconazole ($n > 1$). The one exception to this was soil D with WOEP ($1 > n > 0$). The effect of the formulation on n depended on the soil type, as it was larger for WOEP than for TGP in soils B and C, but smaller in soils A and D. This observation suggested that soils with lower effective cation exchange capacities tended to have larger values of n, especially with WOEP. The high amount of copper in soil D may have had a negative influence on the aggregation number with WOEP. For example, soil D, which contained the highest concentration of total copper (Table 1), had a greater S_{max} and K but a smaller n. This may indicate that high concentrations of copper favor the adsorption of penconazole onto the soil surface but decrease the aggregation number. Penconazole could bind copper to form Cu^{+2}–penconazole complexes [10] with greater affinity for soil colloids than for penconazole itself; but the influence of both copper and soil properties on the aggregation number is not yet fully understood.

4. Conclusions

Phase partitioning of pesticide–soil mixtures using commercial or technical-grade penconazole showed that the sorption of penconazole in the commercial formulation was greater than in the technical grade. About 70% of the total penconazole retained in the solid phase of diluted commercial formulation/soil suspensions was sorbed by soil. Adsorption isotherms of penconazole on soil were well fitted by an S-type model proposed by Gu and Zhu [18] which describes the adsorption including surface aggregation. Exponent values of the average aggregation number $n > 1$ suggested formation of clusters of adsorbed molecules of penconazole. Aggregation or polymerization of penconazole at the non polar sites of soil surface may explain the adsorption in TGP/soil suspensions. Oil–surfactant mixture of the commercial formulation is believed to influence the adsorption of penconazole on soil, by either enhanced penetration of the penconazole onto the less polar sites of the soil

organic matter, or by the co-adsorption of the penconazole within the oil–surfactant mixture.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.05.142.

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