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Influence of the adjuvants in a commercial formulation of the fungicide "Switch" on the adsorption of their active ingredients: Cyprodinil and fludioxonil, on soils devoted to vineyard

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ABSTRACT

The objective of this work was to assess the effect of adjuvants in the sorption in soils of the fungicides, cyprodinil and fludioxonil, usually applied together in a mixture commonly called 'Switch'. Water suspensions of a commercial formulation of Switch were used in phase partition experiments for a set of selected soils from vineyards. A clean-up procedure of the supernatant was developed for the phase separation in presence of the adjuvants prior to quantification of cyprodinil and fludioxonil. The maximum sorption on the solid phase (which includes soil and other solids from the commercial formulation of Switch) was 2000 mg kg^{-1} for fludioxonil and 3000 mg kg^{-1} for cyprodinil after incubation with 800 mg L^{-1} of Switch. However, adsorption to soil particles were lower; fludioxonil concentrations adsorbed in soils range from 50 to 80 mg kg^{-1} of soil and cyprodinil concentrations range from 120 to 260 mg kg^{-1} of soil. Adjuvants increased the solubility of fludioxonil in pure water at 25 °C up to 5 times that of the pure substance (from 1.8 to 9 mg L^{-1} in control samples), and show a strong influence on the adsorption in soil. Soil pH, effective cation exchange capacity and copper content due to past anti fungal copper-based sprays, have also influence on the adsorption of the active ingredients in presence of adjuvants.

1. Introduction

Cyprodinil (4-cyclopropyl-6-methyl-N-phenylpyrimidine) is a systemic fungicide recommended for the prevention and treatment of various fungal diseases that affect fruit, plants and vines. Fludioxonil [4-(2,2,-difluoro-1,3-benzodioxol-4-yl)-1*H*-pyrrole-3-carbonitrile] is a contact fungicide recommended for the control of *Botrytis cinerea* [1]. Both cyprodinil and fludioxonil have low solubility in water, high solubility in non-polar solvents, and high affinity for soil organic matter (SOM). Table 1 shows the values for log *K*ow (octanol/water partition coefficient) and log *K*oc (soil organic carbon/water partition coefficient) for both fungicides. These two fungicides are usually applied together in a mixture commonly called 'Switch', a widely spread formulation that is normally sprayed on the foliage of crops in concentrations from 0.8 to 1 g L^{-1}.

Off-target deposition of pesticides on soil is an environmental concern. The amount of fungicide reached to the soil depends on several factors: the properties of the plant surface, the chemical formulation, application method, and the climate [2], especially the amount of rainfall [2–5]. Less than 0.1% of the pesticide applied to crops actually reaches the target pest; the rest enters the environment [6,7].

Several studies on the sorption behavior of pesticides in soils [6,8] and its correlation with soil properties have been published [9]. Adsorption of cyprodinil and fludioxonil in soils was studied using technical grade standards (high purity level) in batch equilibrium studies [10] at concentrations lower than their solubility limit in water (13 and 1.8 mg L^{-1}, respectively).

Adjuvants are added in commercial formulations [11] to improve the effectiveness and to facilitate spray application [2,12], but also modify the behavior of the active ingredients (AI) in the environment. Previous works reported that decreasing polarity in soil–water suspensions decreases the sorption of cyprodinil [13]. Several works have studied the effect of commercial formulation or cosolvents have in the mobility, increasing in the case of insecticides like endosulfan, or herbicides like ethofumesate, linuron and atrazine or fungicides like metalaxyl [14–16]. Recently, two studies demonstrated that adjuvants play a critical role in the sorption behavior of pesticides in soil. For instance, an increase of about 30% in the metalaxyl retention by soils was observed when the pesticide was applied as a Ridomil Gold Plus formulation rather than the technical grade pesticide [17]. In addition, commercial formulation of penconazole influences the water–soil partition increasing sorp-

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Table 1
Chemical properties of cyprodinil and fludioxonil.

Common name	Chemical name	Log *K*ow	Log *K*oc	p*K*a	Solubility water 25 °C, pH 7 ($mg\,L^{-1}$)
Cyprodinil	(4-Cyclopropyl-6-methyl-N-phenylpyrimidine)	4	3.23	4.4	13
Fludioxonil	[4-(2,2,-Difluoro-1, 3-benzodioxol-4-yl)-1*H*-pyrrole-3-carbonitrile]	4.12	4.87	>14	1.8

Log *K*ow: octanol/water partition coefficient; log *K*oc: soil organic carbon/water partition coefficient.

tion of the pesticide regarding to batch studies using the technical grade AI [18].

The concentrations recommended by the manufacturers for Switch dosage are 300 mg AI L^{-1} for cyprodinil and 200 mg AI L^{-1} for fludioxonil. Therefore, both spray drift and canopy drip reach the soil surface in concentrations higher than the solubility of the AI in water and higher than in ordinary sorption experiments made in laboratory.

The main objective of this work was to study the influence of the adjuvants typically present in the commercial formulation on the sorption of cyprodinil and fludioxonil in soils. We developed experiments using the commercial formulation Switch at the recommended application dosage for a set of selected soils devoted to vineyards. Results were compared with similar partition studies of the same pure AIs reported in previous work.

2. Experimental

2.1. Soil Samples

Composite samples of the top 0–20 cm of the soil were obtained from each of four Rías Baixas vineyards in 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]. All the soils had the same sandy loam texture class, with organic carbon (C) contents that ranged from 3.1 to 4.1% (w/w), clay contents that ranged from 16 to 19% (w/w), a pH_W that ranged from 5.3 to 7.4, and a pH_{KCl} that ranged from 4.6 to 6.6, as listed in Table 2. The pH of soils A and B were less acidic due to the application of lime in the past. The effective cation exchange capacity (ECEC) of the soils ranged from 8.6 to 33.2 ($cmol_{(c)}\,kg^{-1}$), and the total copper (Cu_T) contents ranged from 60 to 274 $mg\,kg^{-1}$; the soils with the higher Cu concentrations experienced repeated applications of Cu-based fungicides.

2.2. Fungicides, standards and solvents

The main characteristics of the commercial formulation of Switch are summarized in Table 3. It was obtained from Syngenta Agro (O Porriño, Spain) as water dispersible granules containing: (i) cyprodinil (37.5%, w/w); (ii) fludioxonil (25%, w/w); and (iii) sodium dibutyl naphthalenesulfonate (SDBNS) $C_{18}H_{23}NaO_3S$ (5%, w/w) in addition to sodium sulphate, ammonium sulphate, calcium carbonate, sodium silicate, and sulphur. The SDBNS is an organic anionic surfactant used as penetrant with a critical micelle concentration (CMC) of 0.02 M in pure water at 25 °C. Penetrants (also called hydrophilic linkers) are amphiphiles that can relax the water bridge network surrounding the hydrophobic sites of surfaces. Its function in commercial fungicides is to enhance the penetration of fungicides through the waxy cuticle onto the leaf tissue [19].

For the sorption experiments with the commercial formulation, a stock standard suspension of commercial Switch (ca. 0.8 $g\,L^{-1}$) was prepared in 0.01 M calcium chloride (pH 6.2) by weighing approximately 0.08 g of Switch into a 100-mL volumetric flask and diluting to volume. Cyprodinil and fludioxonil concentration in this solution was 300 and 200 $mg\,L^{-1}$, respectively, and the concentration of SDBNS in the stock suspension was 0.12 mM, which is less than its CMC.

Technical-grade cyprodinil and fludioxonil were obtained from Riedel-de Haën (Seelze-Hannover, Germany) with purity higher than 90%. A stock standard solution (~1 $g\,L^{-1}$) of each fungicide was prepared in methanol. All standard solutions were stored in the dark at 4 °C and were stable for 6 months.

2.3. Determination of the active ingredients in Switch in the liquid phase

The standard methods used for quantification of high purity cyprodinil and fludioxonil in batch reaction tubes were not suitable for the experiment made with commercial formulations. The supernatant liquid extract had beige-colored turbidity after the phase separation procedure; in addition drift in the detector lead to unacceptable accuracy and precision of measurements. The effect was especially significant for fludioxonil; the readings decreased quickly during the first 24 h; it dropped by about 35% 3 h after centrifugation. Reproducible readings were obtained by purifying the supernatant after centrifugation as follows [2]: an aliquot of the supernatant (5 mL) was passed through a C18 cartridge from Phenomenex (Madrid, Spain) that was previously conditioned with 5 mL of methanol and 10 mL of water. Impurities were removed by washing the cartridge with 5 mL of water; the cartridge was then dried by passing a stream of nitrogen for 20 min. The target compounds were finally eluted with 2.5 mL of a mixture of acetonitrile/water (90/10, v/v) and 50 μL of the eluate was injected into the HPLC to determine the cyprodinil and fludioxonil concentrations in the liquid phase. This purification procedure gave good recovery (about 100%) for both compounds and reproducible readings for two weeks.

Detection and quantification limits (LODs and LOQs) of the method were evaluated on the basis of the noise obtained from the analysis of the soil/0.01 M $CaCl_2$ suspensions without fungicides ($n = 7$), and were defined as the concentrations of the fungicide that produce average signal-to-noise ratios of 3 and 10, respectively. The values obtained for fludioxonil and cyprodinil were 0.1

Table 2
Soil characteristics.

Soil	pH_W	pH_{KCl}	pH_{CaCl2}	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, percentage of organic carbon; ECEC, effective cation exchange capacity ($cmol_{(c)}\,kg^{-1}$); Cu_T, total Cu content ($mg\,kg^{-1}$).

Table 3
Characteristics of commercial product (Switch).

Commercial name	Switch
Commercial brand	Syngenta Agro, S.A.
Composition	Cyprodinil (37.5%, w/w) Fludioxonil (25%, w/w) Sodium dibutyl naphthalenesulfonate (0–5%, w/w)
N CAS	Cyprodinil: 121552-61-2 Fludioxonil: 131341-86-1 Sodium dibutyl naphthalenesulfonate: 25417-20-3
Formulation	Water dispersible granules
Physical characteristics	Granules, light gray to brown
Density of the formula	0.537 g/cm^3
Solubility of the formula	Miscible in water

and 0.2 μg mL^{-1}, respectively, for the LOD and 0.2 and 0.4 μg mL^{-1}, respectively, for the LOQ.

2.4. Quantification of the fungicides

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.

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 and water with the following gradient: 55% of acetonitrile was changed to 90% in 7 min, held for 1 min and then changed to 55% in 0.1 min, giving a total analysis time of 25 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}. Cyprodinil and fludioxonil detection was carried out at 210 nm [20]. The retention times in the chromatogram were 5 and 7 min for fludioxonil and cyprodinil, respectively.

2.5. Switch–water partition

A set of batch experiments were done at different Switch concentrations. In each assay, an amount of the commercial formulation of Switch (8, 20, 40, 80, 200, 400 and 800 mg L^{-1}; corresponding to cyprodinil concentrations ranging from 3 to 300 mg L^{-1} and fludioxonil concentrations ranging from 2 to 200 mg L^{-1}) was suspended in 10 mL of a 0.01 M solution of $CaCl_2$. These suspensions were shaken in a rotating shaker at 200 rpm for 24 h at 25 ± 1 °C in absence of light, after which they were centrifuged for 30 min at 300 × *g*. The pH of the supernatant was measured using a pH-meter. Centrifugation did not remove all the compounds that formed stable colloidal suspensions. Subsequently, a further purification procedure was developed as described in Section 2.3.

Cyprodinil and fludioxonil concentrations obtained for the liquid phase were used as control measures in calculations of the batch sorption equilibrium experiments with soil. All experiments were done in quadruplicate.

2.6. Kinetic experiments

Kinetics experiments were done to determine the equilibrium time in the phase partition of cyprodinil and fludioxonil. Suspensions of the commercial formulation of Switch in 300 mL of 0.01 M $CaCl_2$ (containing 20 mg L^{-1} of cyprodinil and 13.4 mg L^{-1} of fludioxonil) were mixed with 30 g of soil. Suspensions of the commercial formulation with the same concentration of Switch/0.01 M $CaCl_2$ without soil were used as controls. All suspensions were vortex-stirred with a PTFE-coated stir bar at 200 rpm at 25 ± 1 °C, and sampled at 1, 4, 8, 30, 120, 480, 1440, 2880 and 4320 min. Samples were immediately centrifuged for 30 min at 2000 rpm to measure the concentration of fungicide in the supernatant. Kinetic experiments were done in duplicate, two suspensions containing soil and two without soil.

2.7. Fungicide soil batch experiments

Phase partition experiments were done in batch tests using suspensions of the Switch formulation in 0.01 M $CaCl_{2,}$ at concentrations of 8, 20, 40, 80, 200, 400 and 800 mg L^{-1} of Switch (corresponding to cyprodinil concentrations ranging from 3 to 300 mg L^{-1} and fludioxonil concentration from 2 to 200 mg L^{-1}). In each assay, 1 g of soil was suspended in 10 mL of the fungicide mixture; the suspension was shaken in a rotating shaker at 200 rpm at 25 ± 1 °C during the equilibrium time optimized from the kinetic experiments (24 h). After incubation, suspensions were centrifuged for 30 min at 300 × *g*. The concentrations of cyprodinil and fludioxonil, and pH were then determined in the supernatant. Prior to injection in the HPLC system, the supernatant was purified according to the clean-up procedure described in Section 2.3. All experiments were performed in triplicate (n = 3). Control samples (without soil) were also prepared. In all the experiments the quantification of the cyprodinil and fludioxonil concentrations in the liquid phase was carried out as described in Section 2.4.

3. Results and discussion

3.1. Switch–water partition

The maximum cyprodinil and fludioxonil concentrations in 0.01 M $CaCl_2$ suspensions were 300 mg L^{-1} and 200 mg L^{-1}, respectively, corresponding to 800 mg L^{-1} of Switch. These concentrations agree with the recommended dosages for spray application (800–1000 mg L^{-1}). Fig. 1 shows the measured concentration vs. the added concentration for each one of the selected fungicides; a reference line (slope = 1) helps to visualize that, for the highest addictions of Switch, dissolution of the AIs are not complete. Variation in some determinations (e.g. 16–25 mg L^{-1} for cyprodinil) is due to heterogeneity of the commercial product in the water mixture. Cyprodinil measured concentration in the liquid phase reached its solubility limit in water, 20 mg L^{-1} at 25 °C [21]. In contrast, the fludioxonil dissolves up to 9 mg L^{-1}, which is more than the solubility limit of the fungicide in water (1.8 mg L^{-1} at 25 °C [21]).

3.2. Kinetics

The time courses of solubilization and sorption of cyprodinil and fludioxonil in the solid phase are shown in Fig. 2a and b. In control experiments (i.e., Switch suspension without soil) the concentrations of cyprodinil and fludioxonil increased with time, with a little change in concentration after 1440 min (Fig. 2a). Both compounds do not reach complete solubilization at 4320 min. The presence of soil in the suspension decreases the concentration of the AIs in solution with regards to the control at the same incubation times (Fig. 2a and b). Degradation can be neglected because cyprodinil is hydrolytically stable in the pH range 4–9 (half-life in water in the dark is longer than 1 year) [22], and fludioxonil has an average hydrolysis half-life of 30 days in the dark (more than 100 days in presence of soil) [23]. Comparison of the time course of curves of solubilization and sorption to soil suggests that the slow dissolution rate of commercial Switch could be limiting in the sorption kinetics in soil.

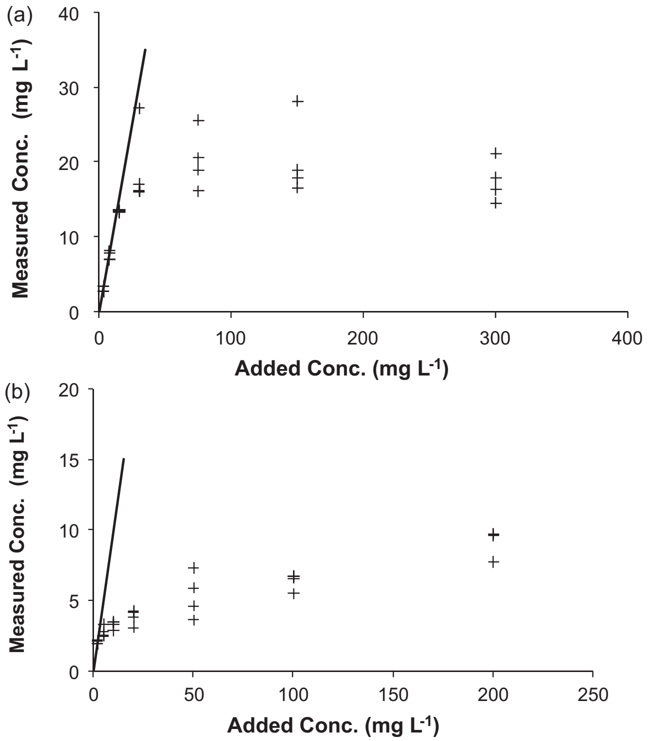

Fig. 1. Solubilization of fungicides in a commercial formulation of Switch/0.01 M $CaCl_2$. Plots show the relationship between the observed and calculated concentrations of (a) cyprodinil and (b) fludioxonil in solution and the reference line that indicates the complete solubilization (slope 1).

3.3. Fungicide soil batch experiments

The addition of the Switch formulation to 0.01 M $CaCl_2$ in absence of soil increases the pH of the suspension (continuous line in Fig. 3). The same additions of Switch have no effect in the pH of the soil/0.01 M $CaCl_2$ suspensions, except in the case of the less acidic soil (soil A), in which pH increases slightly. Acidic soils have a strong buffer effect at low pH by the effect of the exchangeable aluminum and other non crystalline forms of aluminum. Induced changes in the pH of the soil aqueous suspensions by commercial formulations have been reported elsewhere [17,18]. The pH change in the soil solution induced by adjuvants can have significant influence on the sorption of pesticides. This is due to a two-fold effect of pH, first on the variable surface charge of soil, and secondly on the dissociation equilibrium of organic compounds as cyprodinil [6,23].

3.3.1. Phase partition

The commercial formulation of Switch does not dissolve completely in water, therefore suspensions of Switch mixed with soil results in a complex assemblage of phases. In order to evaluate the fludioxonil and cyprodinil partition between the solid and the aqueous phases, the concentration in the solid phase can be calculated as follows:

$$C_{\mathrm{Solid}} = \frac{(C_{\mathrm{Total}} - C_{\mathrm{Liquid}})V}{m} \quad (1)$$

where C_{Solid} (mg kg^{-1}) represents the AI concentration (i.e., cyprodinil or fludioxonil) in the solid phase, C_{Total} (mg L^{-1}) is the calculated concentration resulting the mass of AI added to the liquid phase, C_{Liquid} (mg L^{-1}) is the measured concentration in the liquid phase after incubation, V is the volume of the liquid phase (L), and m is the mass of solids in the suspension (kg). The contribution of

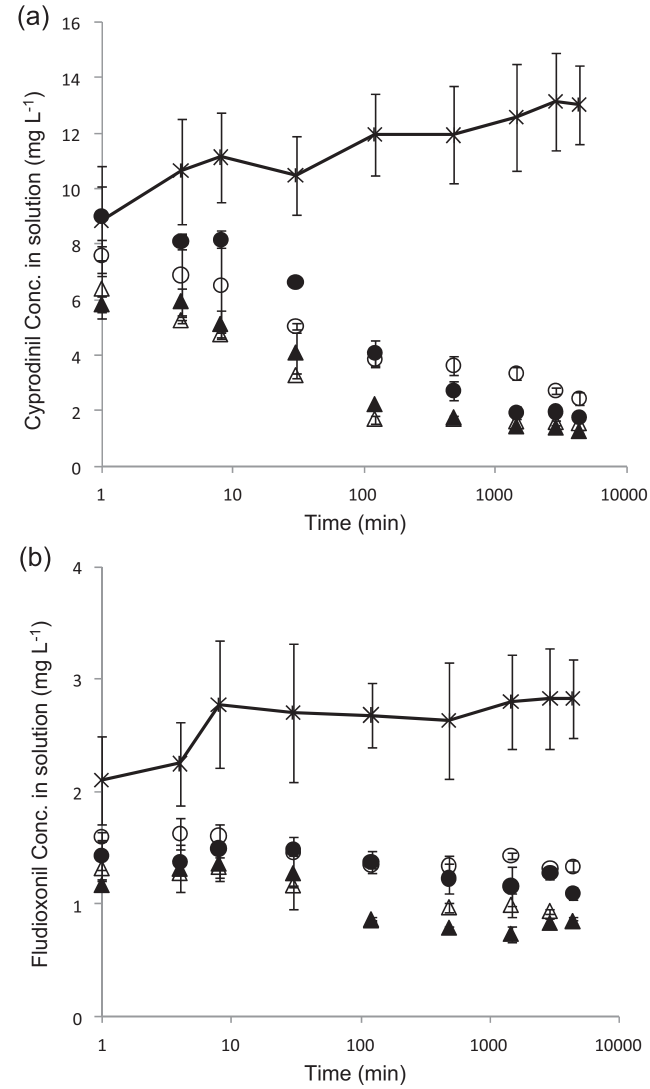

Fig. 2. Time courses of the concentrations in solution of cyprodinil (a) and fludioxonil (b) in kinetic experiments with commercial Switch. The line denotes the control sample and the symbols denote incubation with soil A (◯), soil B (▲), soil C (●) and soil D (△).

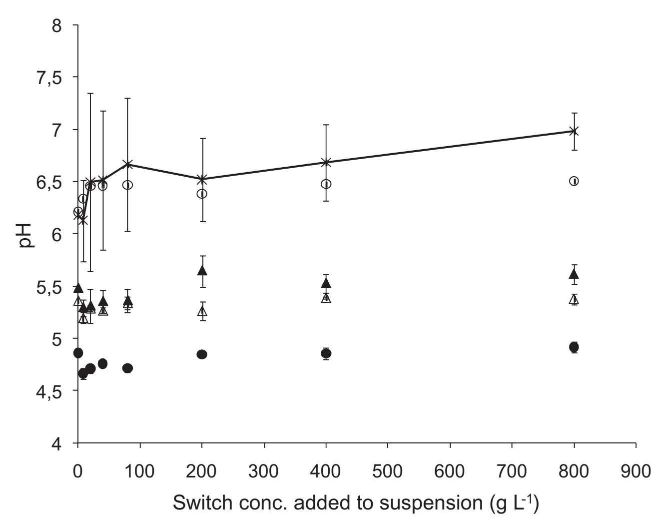

Fig. 3. pH changes in the fungicide/0.01 M $CaCl_2$/soil suspensions induced by the addition of increasing amounts of commercial fungicide after 24 h of incubation. Symbols denote incubation with soil A (◯), soil B (▲), soil C (●) and soil D (△). Line shows the control sample, without soil.

non aqueous ingredients of Switch on m is less than 0.1%, so it is not included in the calculations.

The partition data for cyprodinil and fludioxonil between the solid and the aqueous phases are shown in Figs. 4 and 5, respectively. The maximum sorbed concentration on the total solids is higher for cyprodinil (2500–3000 mg kg^{-1}) than for fludioxonil (1800–2000 mg kg^{-1}). Partition of the AI between the total solids and water can be expressed as a distribution coefficient given by $K_{DT} = C_{Solid}/C_{Liquid}$.

The slope of the sorption curve of cyprodinil in the solid phase is positive for $C_{Liquid} < 15$ mg L^{-1}, with K_{DT} ranging from 40 to 80 L kg^{-1} depending on the soil and the dosage of Switch. When $C_{Liquid} > 15$ mg L^{-1} K_{DT} increases dramatically, that suggests that the concentration of cyprodinil reaches its solubility limit. For the fludioxonil, K_{DT} also increases with the addition of Switch. This behavior would suggest that increasing the concentration of adjuvants favors the sorption of the AIs, but it does not mean that all is adsorbed on soil. In commercial formulation mixtures the AIs retained in the solid phase can precipitate, sorbed onto the non-aqueous adjuvants of the formulation, and/or adsorbed to soil. This is not the typical behavior of high purity AIs in soil–water suspensions, in which the slope of sorption isotherm decreases with concentration.

3.3.2. Adsorption to soil

The concentration of AI adsorbed to soil, C_{Ads}, can be estimated from a pair of batch sorption experiments performed with and without soil, both using the same addition of the Switch, by the following equation:

$$C_{Ads} = \frac{(C_{Control} - C_{Liquid})V}{m} \quad (2)$$

where $C_{Control}$ is the mean AI concentration in solution measured in Switch/0.01 M $CaCl_2$ suspension without soil, C_{Liquid} is the concentration in solution measured in Switch/0.01 M $CaCl_2$ with soil after incubation, V and m are as described above for Eq. (1). This equation assumes that there is no interaction between the adjuvant and the soil that would influence the adsorption of the AI to either the soil or to the adjuvant.

The adsorption curves calculated using Eq. (2) are shown in Figs. 6 and 7. The adsorbed concentration of cyprodinil (Fig. 6) increases with the concentration in solution up to a maximum, and then decreased to values near or below zero. The maximum adsorbed concentrations of cyprodinil in soil are all about 120 mg kg^{-1}, except for soil D showing a maximum adsorption concentration near 260 mg kg^{-1}. Soil D has the greatest concentrations of copper, therefore this soil present less repulsion to the dissociated cyprodinil in solution because the negative surface charge of soil is compensated by the formation of Cu^{2+} inner-sphere complexes. The maximum concentration of cyprodinil adsorbed to soil is 4–8.6% of the total amount of cyprodinil in the solid phase; the rest non-solubilized either precipitated or adsorbed to non-aqueous adjuvants. This behavior of cyprodinil indicates that non-soluble forms of commercial formulations play an important role in the retention of cyprodinil.

This behavior can be discussed on the basis of the solubility limit of cyprodinil in water (20 mg L^{-1} at 25 °C). The first three concentrations assayed are below its solubility limit and the sorbed concentration onto the soil increases with increasing additions of Switch. Thus, it can be concluded that in the case of the soil–water partitions with Switch, sorption of cyprodinil is important only if its concentration is below its solubility limit in water. The distribution coefficients calculated for the soil/liquid partition $K_D = C_{Ads}/C_{Liquid}$ (60–133 L kg^{-1}) for the low concentration range is similar to the K_D observed for the pure ingredient in all soils (61–93 L kg^{-1}) (Table 4) [10]. This finding means that for the low range concentrations, the adsorption mechanisms in presence or absence of adjuvants may not differ. When addition of Switch increases beyond the solubility limit of cyprodinil, other mechanisms can dominate the sorption process. Adsorbed concentrations in soil are observed to decrease to values near or below zero, indicating that the largest amounts of Switch added to soil suspensions decreases the adsorption, even below than in the batch incubations without soil. These results show that there is a threshold concentration of Switch that decreases the adsorption of cyprodinil to soil. In addition, presence of soil in the Switch suspension enhances solubilization of cyprodinil.

Table 4
Comparison of the distribution coefficients for the soil/water partition (K_D, L kg^{-1}) for between selected intervals of the adsorption curves of cyprodinil and fludioxonil added as Switch and values from the literature. 'Low range' is where the dissolved concentration is below the solubility limit of the pure active ingredient in water at 25 °C. 'High range' is up to the concentration resulting the dilution of Switch recommended by the manufacturer.

Soil	Low range	High range	Reported in [10]
Fludioxonil			
	(<0.2 mg L^{-1})	(0.2–4.5)	(<0.2)
A	65	10.	116
B	86	8.	129
C	18	20	110
D	123	8	187
Cyprodinil			
	(3–15 mg L^{-1})	(15–25)	(<13)
A	60	n.d.	61
B	133	n.d.	82
C	97	n.d.	79
D	107	n.d.	93

The adsorbed concentration of fludioxonil increases with the addition of Switch (Fig. 7). For soils A, B and D, the first point on the adsorption curves is near C_{Ads} 18 mg kg^{-1}; the slope from the origin to the first experimental point corresponds to an approximate linear distribution K_D in the range from 65 to 123 L kg^{-1}. For low additions of Switch K_D is similar to the partition of pure compounds reported by [10] (Table 4). With higher additions (i.e., $C_{Liquid} > 1$ mg L^{-1}) K_D values are smaller than those found for the adsorption of the analytical grade fludioxonil. That suggests an increased solubilization of the fludioxonil by the adjuvants. For medium additions of Switch (i.e., when C_{Liquid} is 1–2 mg L^{-1}) the adsorption of fludioxonil decreases slightly. With larger additions of Switch the adsorption increased dramatically. Maximum C_{Ads} is in the range from 50 to 60 mg kg^{-1}. Soil C shows the greater sorbed concentration $C_{Ads} = 80$ mg kg^{-1}, but this is only the 2.5% of the mass of fludioxonil added.

These adsorption curves are difficult to include in a particular isotherm model because partition occurs in a complex system formed by soil, water, the AIs and adjuvants.

3.3.3. Influence o surfactant on adsorption

The interpretation of the batch adsorption curves for Switch could be explained by two potential effects: the first one is the formation of hemimicellization of SDBNS on the soil surface followed by the co-adsorption of the pesticide with the hemimicelles [18], and secondly the role of SDBNS as penetrant in the non polar sites of soil organic matter (SOM). The mechanism of penetration in SOM is that hydrophobic tail of SDBNS can enters to internal non-polar sites and its polar head fits between the hydrophilic functional groups of the SOM. Therefore, SDBNS would decrease the attractive forces in the hydrogen bridge network surrounding the SOM, and the fungicide can coadsorb with SDBNS at the polar–non polar interface. The effectiveness of both mechanisms will depend upon the electrostatic repulsion between the surfactant and SOM surface. Low pH of the soil solution and complexation

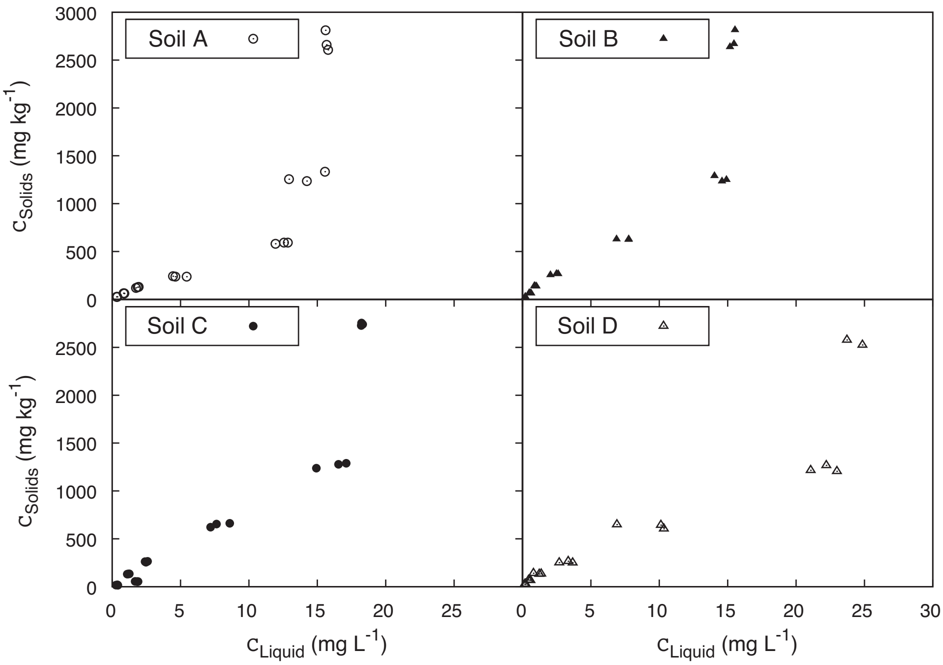

Fig. 4. Partition phase equilibrium of cyprodinil in commercial fungicide/0.01 M $CaCl_2$/soil suspensions, soil A (○), soil B (▲), soil C (●) and soil D (△). C_{Solids} denote the sorbed concentration of cyprodinil on total suspended solids (soil and adjuvants), and C_{Liquid} the concentration in solution.

of copper by the SOM decreases the negative charge surface of SOM, these factors diminish the repulsion of SDBNS, and therefore can explain the greater adsorption of cyprodinil in the soil D (Fig. 6).

The influence of SDBNS can also help to explain the local minimum of adsorption of fludioxonil at C_{Liquid} 1–2 mg L^{-1} (Fig. 7). There is a point at which the more accessible and favorable sites for adsorption have been already filled by fludioxonil (this can be seen as a local maximum near C_{Ads} = 20 mg kg^{-1}); further additions of Switch to the suspension enhance solubilization, as observed in controls (i.e., without soil), causing a decrease in C_{Ads}. Even highest addition of Switch adds more SDBNS which facilitates the co-hemimicellization or penetration of the fludioxonil into the less polarity sites in the SOM.

Comparing the curves of cyprodinil and fludioxonil (Figs. 6 and 7), it is observed that the adsorption of fludioxonil increased with the addition of large quantities of Switch while that adsorption of cyprodinil decreased. The less water-soluble fludioxonil is more effective at adsorbing in the non-polar sites of SOM than cyprodinil. We speculate that with the highest additions

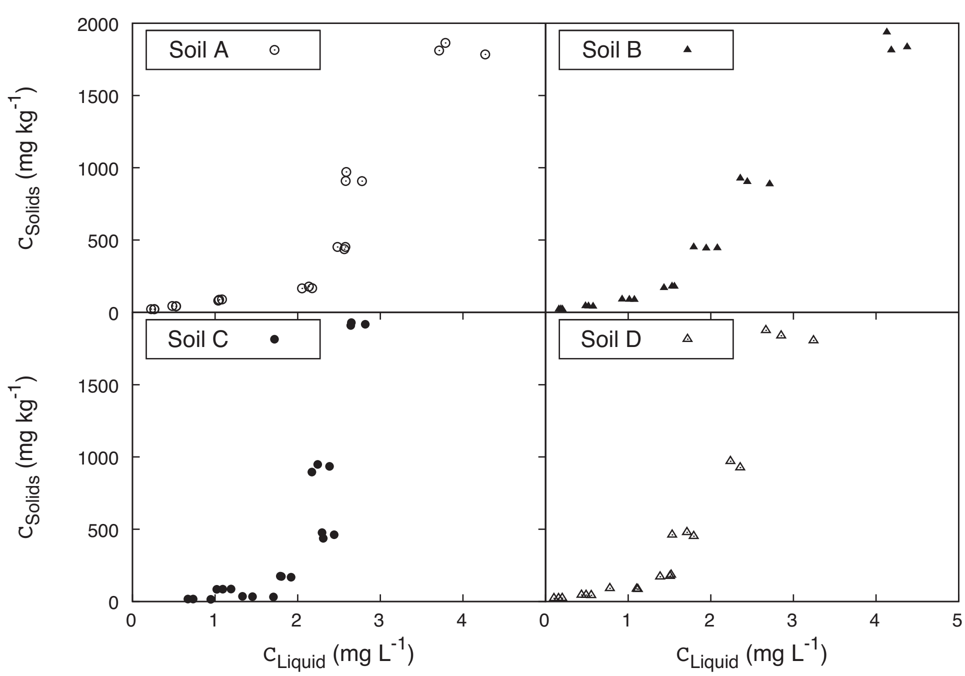

Fig. 5. Partition phase equilibrium of fludioxonil in commercial fungicide/0.01 M $CaCl_2$/soil suspensions, soil A (○), soil B (▲), soil C (●) and soil D (△). C_{Solids} denote the sorbed concentration of fludioxonil on total suspended solids (soil and adjuvants), and C_{Liquid} the concentration in solution.

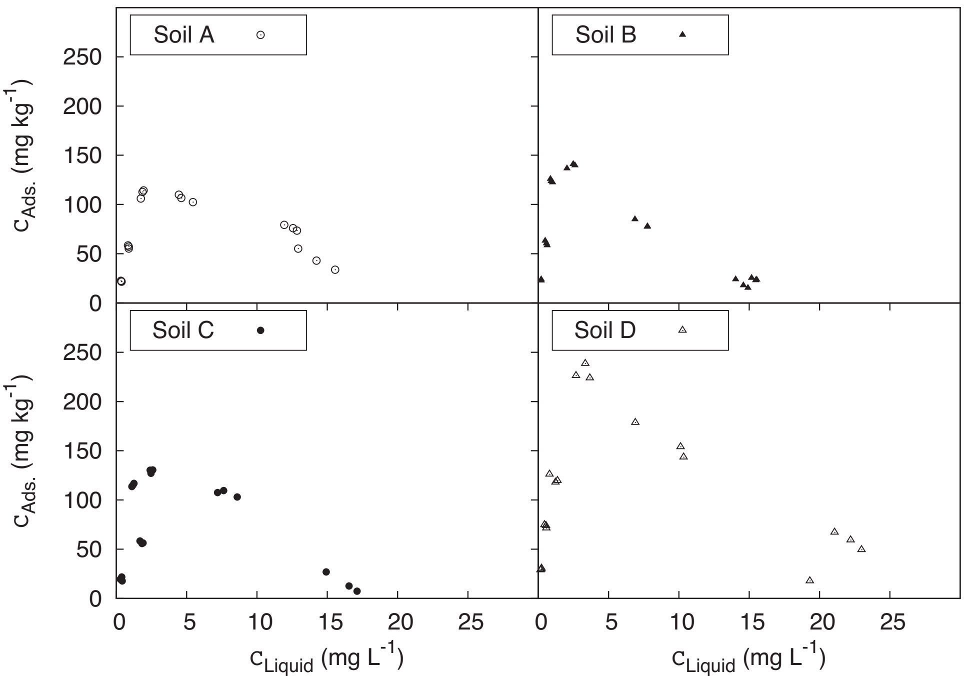

Fig. 6. Adsorption equilibrium of cyprodinil in soil after incubations of commercial fungicide in 0.01 M $CaCl_2$/soil suspensions, soil A (○), soil B (▲), soil C (●) and soil D (△). C_{Ads} denote the adsorbed concentration of fludioxonil on total suspended solids (soil and adjuvants), and C_{Liquid} the concentration in solution.

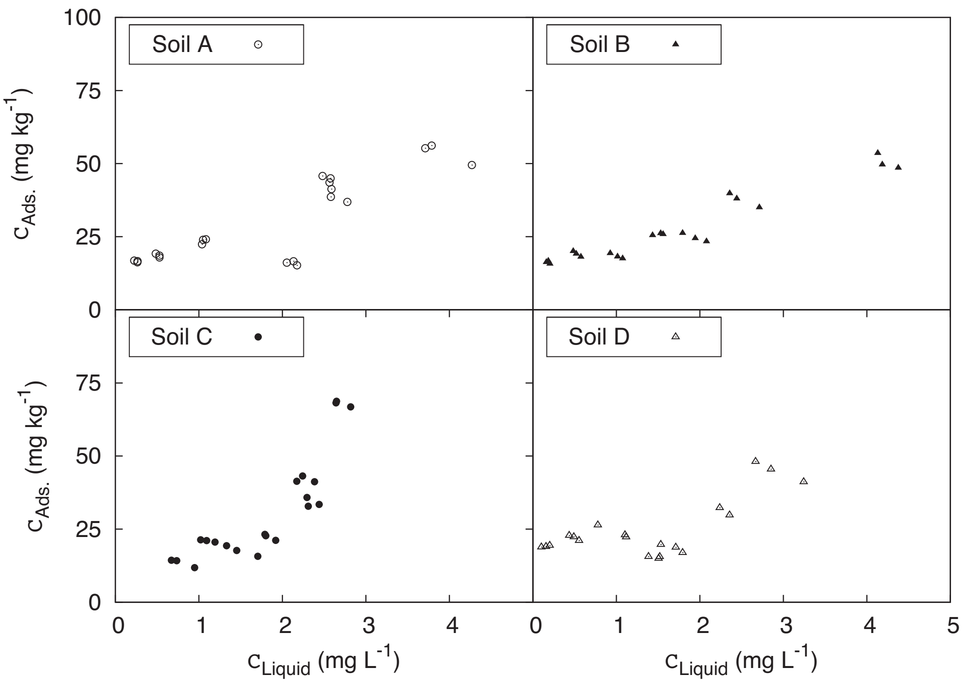

Fig. 7. Adsorption equilibrium of fludioxonil in soil after incubations of commercial fungicide in 0.01 M $CaCl_2$/soil suspensions, soil A (○), soil B (▲), soil C (●) and soil D (△). C_{Ads} denote the adsorbed concentration of fludioxonil on total suspended solids (soil and adjuvants), and C_{Liquid} the concentration in solution.

of Switch, the increased concentration of SDBNS difficult the adsorption of cyprodinil on soils.

4. Conclusions

The sorption of cyprodinil and fludioxonil, applied as Switch commercial formulations, was studied in vineyard-devoted soils in the range of concentrations recommended by the manufacturer (0.8–1 g L^{-1}). The adjuvants present in the commercial formulation increase the concentration of fludioxonil in water suspensions up to 9 mg L^{-1}, which by about 5 times that of its solubility limit in water (1.8 mg L^{-1}). Solubilization of cyprodinil is not increased by adjuvants. Adjuvants increased the pH in the suspensions of the acidic soils, but the influence was negligible for limed soil. Soil pH, effective cation exchange capacity of soil, and soil copper content due to anthropogenic inputs, have also influence on the sorption of Switch's fungicides. The low pH in the more acidic soils favors the adsorption of fludioxonil.

The commercial formulation has a strong influence on the soil water partition tests. Adjuvants contribute to enhance the overall sorption of cyprodinil and fludioxonil. However, at high concentrations of Switch, adjuvants can limit cyprodinil adsorption to soil.

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