

# Application of a biosorbent to soil: a potential method for controlling water pollution by pesticides

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**Abstract** Different strategies are now being optimized to prevent water from agricultural areas being contaminated by pesticides. The aim of this work was to optimize the adsorption of non-polar (tebuconazole, triadimenol) and polar (cymoxanil, pirimicarb) pesticides by soils after applying the biosorbent spent mushroom substrate (SMS) at different rates. The adsorption isotherms of pesticides by three soils and SMS-amended soils were obtained and the adsorption constants were calculated. The distribution coefficients ( $K_d$ ) increased 1.40–23.1 times (tebuconazole), 1.08–23.7 times (triadimenol), 1.31–42.1 times (cymoxanil), and 0.55–23.8 times (pirimicarb) for soils amended with biosorbent at rates between 2 and 75 %. Increasing the SMS rates led to a constant increase in adsorption efficiency for non-polar pesticides but not for polar pesticides, due to the increase in the organic carbon (OC) content of soils as indicated by  $K_{OC}$  values. The OC content of SMS-amended soils accounted for more than 90 % of the adsorption variability of non-polar pesticides, but it accounted for only 56.3 % for polar pesticides. The estimated adsorption of SMS-amended soils determined from the individual adsorption of soils and SMS was more consistent with real experimental values for non-polar pesticides than for polar pesticides. The results revealed the use of SMS as a tool to optimize pesticide adsorption

by soils in dealing with specific contamination problems involving these compounds.

**Keywords** Biosorbent · Spent mushroom substrate · Immobilization · Soil · Non-polar pesticides · Polar pesticides · Water pollution

## Introduction

The waste material called spent mushroom substrate (SMS) is the soil-like material remaining after a crop of mushrooms has been harvested. The production of 1 kg of mushroom produces 5 kg of SMS. China has the largest production in the world (20 Mt) (Phan and Sabaratnam 2012). In addition, the USA, Netherlands, France, Ireland, Poland, and Spain are currently major producers (FAOSTAT 2015).

In Spain, mushroom production represented about 7.63 % of the entire European Union (EU) production in 2012 (FAOSTAT 2015). In the region of La Rioja, increasing quantities of SMS are being produced (about 170,000 t of SMS per year) (MAGRAMA 2015). It has been reported that the SMS addition to a semiarid vineyard soil in this region could be a promising strategy for the sustainable recycling of this waste avoiding its ultimate disposal in landfills. The SMS addition increases the organic matter (OM) of these soils with low OM content, which have beneficial effects on soil quality, especially on soil biochemical properties and microbiological parameters (Medina et al. 2012; Peregrina et al. 2012).

Besides these potential benefits, SMS has a major ability to adsorb pesticides from water (Marín-Benito et al. 2012a). The role it plays in controlling the behavior of the pesticides applied, or which enter the soil along with the SMS, has been investigated. The OM applied with the SMS might influence the sorption capacity of pesticides by soils and modify their

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concentration in the soil solution, decreasing their toxic effects (Gómez et al. 2014). Studies have focused especially on the influence on the adsorption and degradation of certain fungicides frequently used in vineyards depending on the nature of the SMS, as determined by its degree of composting, or the length of time the soil has been incubated with the waste (Marín-Benito et al. 2012b). The results obtained following the application of SMS to the soil have revealed a decrease in adsorption over the waste's incubation time with the soil, and the influence of SMS organic carbon (OC) and dissolved organic carbon (DOC) on the adsorption and dissipation processes of relatively hydrophobic fungicides. The more hydrophobic pesticides recorded a significant increase in adsorption by the SMS-amended soil, even at a dose of 2 %, although the presence of this waste was not so efficient for the adsorption of less hydrophobic pesticides.

Nevertheless, in view of the current interest in avoiding the contamination of groundwater due to the leaching of the pesticides that reach the soil, it was considered expedient to discover whether the application to the soil of different SMS rates may allow optimizing the adsorption of different kinds of pesticides depending on the need to address specific environmental issues. Pesticides are organic compounds that are widely used in high amounts in order to increase the quality and yield of crops. Their presence in waters in concentrations higher than those allowed by legislation on drinking water (Directive No. 2008/105/EC, amending the Water Framework Directive 2000/60/EC) is becoming more common (Herrero-Hernández et al. 2013; Masiá et al. 2015). These concentrations in the water may come from diffuse contamination due to the agricultural use of these compounds, although in many cases, they have been attributed to point soil contamination due to the improper disposal of empty containers or the washing of equipment after the pesticide's application (Fait et al. 2007).

Good agro-environmental practices have been proposed to avoid diffuse contamination, while biobeds or biomix systems have been described for avoiding point contaminations (Castillo et al. 2008). In both cases, the application and/or use of wastes from different origins with a high percentage of OM in their composition is of great interest for avoiding environmental pollution in the most cost-effective ways possible (Beesley et al. 2011). The adsorption of pesticides by the OM of the residues has an effect on their degradation rate and bioavailability and determines the concentration of pesticides in the soil solution and how they are transported throughout the medium (Dolaptsoglou et al. 2007; Rodríguez-Salgado et al. 2014). Accordingly, adsorption studies are a good method for measuring the adsorbent capacity of the modified soil by the addition of wastes from different origins. After pesticides have been sequestered in the amended soil, they could remain in the soil as chemically adsorbed, physically trapped, or a combination of both processes (Zhang et al. 2011; Ahmad

et al. 2014), thus decreasing the likelihood of being leached (Fenoll et al. 2015; Kodešová et al. 2011).

The fungicides tebuconazole, triadimenol, and cymoxanil are widely used in vineyards to combat powdery mildew fungi, and pirimicarb is an insecticide used to control aphids. These pesticides could reach the soil after their application to plants, and we have detected them in groundwaters in the region of La Rioja (Herrero-Hernández et al. 2013).

The aims of this study are to evaluate the capacity of a SMS-amended soil to adsorb two non-polar pesticides (tebuconazole and triadimenol) and two polar pesticides (cymoxanil and pirimicarb) with different hydrophobic character and water solubility, and determine the effect that different rates of biosorbent have on the immobilization of these pesticides. The adsorption of these compounds by three soils amended with SMS at different rates was carried out in order to discover the following: (i) the effect of SMS when applied to soil as an organic amendment (lower rates 2–10 %) on the adsorption of pesticides used in agricultural practices, and (ii) the effect of SMS when applied to soil as a barrier (higher rates, 25–75 %) on the adsorption/immobilization of pesticides to prevent the pollution of groundwater.

## Materials and methods

### Chemicals

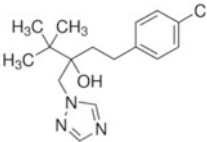
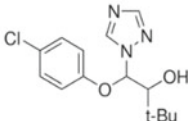
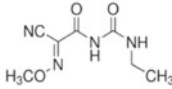
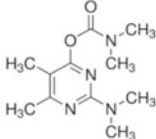
Pesticides studied were three fungicides (tebuconazole, cymoxanil, and triadimenol) and one insecticide (pirimicarb). Table 1 shows their characteristics (PPDB 2015). Two pesticides selected are classified as non-polar and immobile (tebuconazole) or mobile (triadimenol) and two more pesticides are classified as polar and immobile (pirimicarb) or mobile (cymoxanil) according to the classification of non-polar when the  $\log K_{ow}$  value is  $>3.0$  and as mobile when the  $\log K_{OC}$  is  $<2.5$  (Delle Site 2001).

Tebuconazole and cymoxanil were used  $^{14}C$ -labelled with specific activity and purity of  $4.72 \text{ MBq mg}^{-1}$  and  $98.1 \%$  for  $^{14}C$ -tebuconazol and  $10.08 \text{ MBq mg}^{-1}$  and  $97.79 \%$  for  $^{14}C$ -cymoxanil. Both pesticides were supplied by IZOTOP (Hungary). Unlabelled pesticides (purity  $>98 \%$ ) were supplied by Sigma-Aldrich Química SA (Madrid, Spain).

### Biosorbent and soils

Biosorbent spent mushroom substrate (SMS) from *Agaricus bisporus* cultivation was supplied by Sustratos de La Rioja S.L. (Pradejón, Spain). Its composition was described by Marín-Benito et al. (2012b), and their physicochemical characteristics determined as described in this previous work are as follows: pH was 6.97, ash content was 33.6 %, OC content was 24.5 %, DOC was 1.91 %, and moisture content was 64.5 %.

**Table 1** Chemical structure and physicochemical properties of pesticides studied

Common name IUPAC name	Chemical structure	WS (mg L <sup>-1</sup> )	Log Kow	Koc (mL g <sup>-1</sup> )	DT <sub>50</sub> (days <sup>-1</sup> )	GUS index
Tebuconazole ( <i>RS</i> )-1- <i>p</i> -chlorophenyl- 4,4-dimethyl-3-(1 <i>H</i> - 1,2,4-triazol-1- ylmethyl)pentan-3-ol		36	3.7	769	63-365	2.0
Triadimenol (1 <i>RS</i> ,2 <i>RS</i> ;1 <i>RS</i> ,2 <i>SR</i> )-1- (4-chlorophenoxy)-3,3- dimethyl-1-(1 <i>H</i> -1,2,4- triazol-1-yl)butan-2-ol		72	3.18	273	64.9-250	3.75
Cymoxanil 1-[( <i>EZ</i> )-2-cyano-2- methoxyiminoacetyl]-3- ethylurea		780	0.67	43.6	0.7-3.5	-0.37
Pirimicarb 2-dimethylamino-5,6- dimethylpyrimidin-4-yl dimethylcarbamate		3100	1.7	388	86	2.73

From PPDB, Pesticide Properties DataBase (2015) <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>. *WS*, solubility in water at 20 °C; *K<sub>ow</sub>*, octanol/water partition coefficient at pH 7 and 20 °C; *K<sub>OC</sub>*, sorption coefficient normalized to organic carbon content

Soil samples were collected from the surface horizon (0–30 cm in three vineyards in La Rioja region (Spain) located in Alcanadre (ALC, 42° 24' 20" N, 2° 7' 6" W) in La Rioja Baja, Sajazarra (SJZ, 42° 35' 18" N, 2° 57' 41" W), and Yécora (YEC, 42° 32' 47" N, 3° 5' 48" W) both in La Rioja Alta. The soils were air-dried and sieved (<2 mm) to determine their characteristics using standard analytical methods (MAPA 1986). Soils selected had low OM contents and different clay contents. Their textures were classified as sandy loam, sandy clay loam, and clay loam, respectively.

Soils were amended with the biosorbent by uniformly mixing of soil with appropriate amounts of SMS sieved (<2 mm) to obtain rates of 2, 5, 10, 25, 50, and 75 % (*w/w*), on a dry weight basis. The initial moisture content of all soils was adjusted to 40 % of their maximum water holding capacity. Adsorption assays were conducted after some days of SMS-soil incubation to equilibrate. Characteristics of unamended and amended soils are included in Table 2.

### Adsorption experiments

Adsorption isotherms of pesticides by unamended and amended soils were obtained using the batch equilibrium technique. Adsorption of tebuconazole and cymoxanil was carried

out by ALC, SJZ, and YEC soils and adsorption of triadimenol and pirimicarb was carried out by ALC and SJZ soils. Duplicate soil samples (1 g) were equilibrated with 10 mL of a Milli-Q ultrapure water solution of each pesticide at concentrations of 1, 5, 10, 15, 20, and 25 µg mL<sup>-1</sup> for non-polar pesticides and 1, 5, 10, 15, 20, 25, 50, and 100 µg mL<sup>-1</sup> for polar pesticides, according to the solubility range of compounds. The soil/solution ratio was adapted to obtain a suitable adsorption according to the OECD guideline (OECD/OCDE 2000). An activity of 100 Bq mL<sup>-1</sup> was used for <sup>14</sup>C-tebuconazole and <sup>14</sup>C-cymoxanil. The suspensions were shaken at 20±2 °C for 24 h in a thermostated chamber, with intermittent shaking for 2 h at 3-h intervals. Preliminary experiments revealed that contact for 24 h was long enough for attaining equilibrium. The suspensions were subsequently centrifuged at 5045g for 15 min, and the equilibrium concentration of each pesticide was determined. The amount of pesticide adsorbed was calculated as the difference between that initially present in solution and that remaining after equilibration with the soil. Blanks (soils without pesticide or standard solutions without soil) were prepared and managed in a similar way to samples and used as controls. Calculations were based on the assumption that no degradation of fungicides occurred during sorption studies.

**Table 2** Characteristics of unamended and amended soils

Soil	pH	OC %	DOC %	OM %	N %	C/N	CO <sub>3</sub> <sup>2-</sup> %	Sand %	Silt %	Clay %	Clay mineralogy <sup>a</sup>
ALC	7.49	0.89	<0.01	1.53	0.10	9.10	24.1	79.6	9.0	11.4	I, K, V
ALC+SMS2	7.39	1.22	0.056								
ALC+SMS5	7.26	2.22	0.062								
ALC+SMS10	7.22	4.00	0.277								
ALC+SMS25	7.15	7.11	0.342								
ALC+SMS50	7.10	15.6	0.446								
ALC+SMS75	7.06	18.9	1.063								
SJZ	7.52	0.67	<0.01	1.15	0.06	12.3	50.9	67.0	11.9	21.1	I, K
SJZ+SMS2	7.40	0.97	0.042								
SJZ+SMS5	7.26	1.73	0.062								
SJZ+SMS10	7.25	3.56	0.199								
SJZ+SMS25	7.21	6.25	0.399								
SJZ+SMS50	7.19	16.3	0.439								
SJZ+SMS75	7.09	17.6	1.211								
YEC	7.84	1.00	<0.01	1.72	0.09	10.4	12.9	34.6	29.7	35.7	I, K, M
YEC+SMS2	7.70	1.78	0.038								
YEC+SMS5	7.46	2.22	0.047								
YEC+SMS10	7.56	4.89	0.169								
YEC+SMS25	7.36	9.33	0.454								
YEC+SMS50	7.29	12.2	0.442								
YEC+SMS75	7.59	19.3	0.840								

<sup>a</sup> Illite (I), kaolinite (K), montmorillonite (M), vermiculite (V)

**Pesticide analysis**

The equilibrium concentrations of <sup>14</sup>C-tebuconazole and <sup>14</sup>C-cymoxanil in the supernatant were determined by liquid scintillation counting on a Beckman LS6500 liquid scintillation counter (Beckman Instrument Inc., Fullerton, CA). The radioactivity of the equilibrium solution was measured in disintegrations per minute (dpm) as indicated in Marín-Benito et al. (2012b).

Pirimicarb and triadimenol were determined by HPLC-MS (Waters Association, Milford, MA), using a Phenomenex Luna (3 μ C18, 150 × 4.60 mm) column. The mobile phase was in both cases 80:20 (v/v) acetonitrile/water (0.1 % formic acid). The flow rate was 0.3 mL min<sup>-1</sup>, and the sample injection volume was 20 μL. Calibration curves were generated between 0.1 and 100 μg mL<sup>-1</sup> (pirimicarb) and between 0.1 and 25 μg mL<sup>-1</sup> (triadimenol) concentrations of standards in solutions of adsorbent extracts to counteract any possible matrix effect. Retention times for pirimicarb and triadimenol were 4.5 and 5.1 min, respectively. Quantitative analysis was performed using the peak area of each compound obtained from the total ion chromatogram in SIM mode. The positive molecular ion (*m/z*) was 239.29 for pirimicarb and 296.76 for triadimenol. The limits of detection (LOD) were 0.014 and 0.011 μg L<sup>-1</sup>, and the limits of quantification (LOQ) were 0.039 and 0.036 μg L<sup>-1</sup> for pirimicarb and triadimenol, respectively.

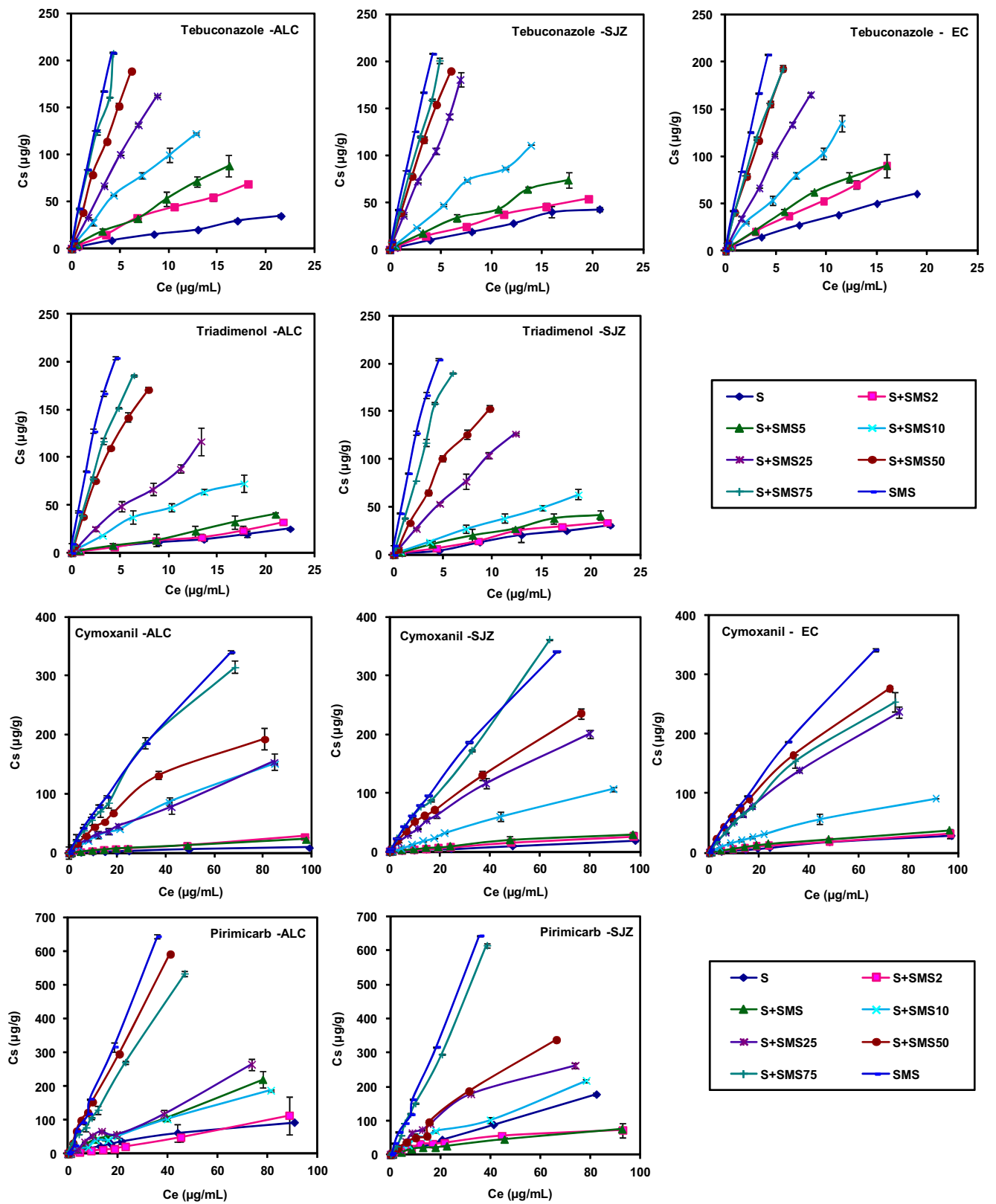
**Data analysis**

Pesticide adsorption data were fitted to the Freundlich equation  $C_s = K_f C_e^{nf}$ , where  $C_s$  (μg g<sup>-1</sup>) is the amount of adsorbed pesticide,  $C_e$  (μg mL<sup>-1</sup>) is the equilibrium concentration of pesticide solution, and  $K_f$  (μg<sup>1-nf</sup> g<sup>-1</sup> mL<sup>nf</sup>) and  $nf$  are the Freundlich adsorption and non-linearity coefficients, respectively. Distribution coefficients,  $K_d$  (mL g<sup>-1</sup>), were determined from the relationship between  $C_s$  and  $C_e$ , and  $K_d$  values normalized to 100 % OC ( $K_{OC}$ ) were calculated. Standard deviation (SD) was used to indicate variability in the adsorption coefficients among replicates. Simple and multiple linear regression models were used to relate adsorption to the soil characteristics. IBM SPSS (version 22; USA) statistical software was used.

**Results and discussion**

**Effect of different rates of SMS on the adsorption of non-polar pesticides**

Figure 1 includes the adsorption isotherms of tebuconazole and triadimenol for unamended soils, SMS, and soils amended with rates of SMS in the 2–75 % range. All the isotherms fitted the Freundlich equation, with *r* values ≥0.99



**Fig. 1** Adsorption isotherms of non-polar and polar pesticides by unamended soils, SMS, and amended soils at different SMS rates. Error bars represent the standard deviation of the  $C_s$  mean value ( $n=2$ )

and  $\geq 0.95$ , respectively.  $K_f$  and  $nf$  parameters were determined from the linear form of this equation, and they are included in Table 3. The adsorption isotherms of tebuconazole for unamended soils were non-linear (L-type), although an increasing linearity was seen for the isotherms of fungicide for soils amended at different rates. These isotherms indicated that adsorption decreases at high concentrations of pesticide in solution. Similar non-linear shapes were obtained for the adsorption isotherms of triadimenol for unamended and amended soils, although the increase in linearity was less significant. Adsorption and partitioning mechanisms may explain the retention of these non-polar pesticides as a function of the rates of SMS in the soils. These adsorption mechanisms have been reported for the adsorption of other non-polar pesticides or organic contaminants by amended soils with different organic materials (Eibisch et al. 2015).

$K_f$  values for the adsorption of tebuconazole and triadimenol by unamended soils were in the 2.55–5.03 and 1.69–1.81 range, respectively, and 53.8 and 57.9, respectively, for SMS. OC increased after the SMS amendment of soils and enhanced the adsorption of both pesticides by SMS-amended soils, with the increased soil adsorption of tebuconazole being

higher than that of triadimenol (Table 3). Significant correlation coefficients were found between  $K_f$  values and OC contents of soils ( $r$  ranged between 0.978 and 0.992 for tebuconazole and between 0.953 and 0.978 for triadimenol ( $p < 0.01$ )). DOC also increased after the SMS amendment of soils, and a positive significant correlation was recorded between  $K_f$  and DOC of soils ( $r = 0.903$ – $0.918$  for tebuconazole ( $p < 0.05$ ) and  $r = 0.994$ – $0.977$  for triadimenol ( $p < 0.01$ )). A significant correlation coefficient was found between OC and DOC, although DOC did not decrease the adsorption of these pesticides by amended soils, as observed for other organic residues and/or pesticides. Reports have indicated increases or decreases in the adsorption of pesticides by soils because of the effect of DOC (Andrades et al. 2004; Rodríguez-Cruz et al. 2012). In this case, soluble organic compounds could be adsorbed by soil components, giving rise to the formation of new hydrophobic surfaces that would increase pesticide adsorption.

The  $K_d$  distribution coefficients were determined at an equilibrium concentration of  $5 \mu\text{g mL}^{-1}$  to compare the adsorption capacity of pesticides by soils amended with different rates of SMS (2–75 %), because the  $nf$  values of the adsorption

**Table 3** Freundlich adsorption constants and distribution coefficients of non-polar pesticides by soils amended at different SMS rates

Soil	Tebuconazole				Triadimenol			
	$K_f \pm \text{SD}^a$	$nf \pm \text{SD}$	$K_d 5^b \pm \text{SD}$	$K_{OC}$	$K_f \pm \text{SD}$	$nf \pm \text{SD}$	$K_d 5 \pm \text{SD}$	$K_{OC}$
ALC	2.55 ± 0.26	0.84 ± 0.03	1.99 ± 0.11	224	1.81 ± 0.82	0.83 ± 0.11	1.36 ± 0.11	153
ALC + SMS2	4.94 ± 0.01	0.92 ± 0.03	4.34 ± 0.39	356	1.63 ± 1.01	0.94 ± 0.18	1.46 ± 0.46	120
ALC + SMS5	6.76 ± 0.28	0.90 ± 0.02	5.73 ± 1.54	258	2.41 ± 0.94	0.88 ± 0.14	1.99 ± 0.80	89.7
ALC + SMS10	13.5 ± 0.93	0.89 ± 0.01	11.2 ± 3.21	281	6.45 ± 1.02	0.87 ± 0.02	5.26 ± 0.05	132
ALC + SMS25	20.0 ± 0.03	0.98 ± 0.00	19.8 ± 0.49	271	9.11 ± 1.36	0.97 ± 0.01	8.74 ± 1.21	123
ALC + SMS50	34.6 ± 0.64	0.94 ± 0.02	31.5 ± 2.22	202	25.4 ± 0.32	0.93 ± 0.01	22.6 ± 2.36	145
ALC + SMS75	48.9 ± 1.77	0.96 ± 0.02	45.9 ± 2.57	243	34.3 ± 3.55	0.96 ± 0.04	32.3 ± 1.62	171
SJZ	3.06 ± 0.06	0.89 ± 0.01	2.57 ± 0.10	383	1.69 ± 0.43	0.92 ± 0.05	1.50 ± 0.25	224
SJZ + SMS2	4.71 ± 0.67	0.83 ± 0.07	3.60 ± 0.55	371	2.32 ± 0.78	0.88 ± 0.11	1.75 ± 0.41	180
SJZ + SMS5	6.24 ± 0.04	0.87 ± 0.01	5.03 ± 1.36	290	3.08 ± 0.94	0.88 ± 0.11	2.54 ± 0.35	147
SJZ + SMS10	9.16 ± 0.78	0.96 ± 0.02	8.61 ± 0.79	242	4.71 ± 0.31	0.87 ± 0.02	3.88 ± 0.48	109
SJZ + SMS25	26.9 ± 1.59	0.95 ± 0.03	24.9 ± 5.77	398	10.9 ± 0.59	0.99 ± 0.00	10.6 ± 1.02	169
SJZ + SMS50	36.6 ± 0.38	0.94 ± 0.00	33.1 ± 0.29	203	18.9 ± 0.83	0.98 ± 0.05	18.1 ± 1.96	111
SJZ + SMS75	42.0 ± 0.05	0.97 ± 0.00	39.9 ± 0.41	226	35.6 ± 3.01	0.90 ± 0.09	34.4 ± 2.47	195
YEC	5.03 ± 0.02	0.84 ± 0.02	3.91 ± 0.08	391				
YEC + SMS2	7.10 ± 0.05	0.90 ± 0.00	6.07 ± 0.30	341				
YEC + SMS5	8.17 ± 0.23	0.90 ± 0.04	6.93 ± 0.72	312				
YEC + SMS10	13.9 ± 0.14	0.92 ± 0.02	11.9 ± 0.20	245				
YEC + SMS25	21.6 ± 0.98	0.96 ± 0.06	20.2 ± 1.42	216				
YEC + SMS50	38.2 ± 1.46	0.93 ± 0.01	35.4 ± 0.28	290				
YEC + SMS75	40.5 ± 0.34	0.95 ± 0.02	36.3 ± 0.68	188				
SMS	53.8 ± 1.32	0.95 ± 0.01	49.9 ± 4.62	203	57.9 ± 0.58	0.90 ± 0.03	48.9 ± 7.90	199

<sup>a</sup> SD, standard deviation ( $n = 2$ )

<sup>b</sup> Distribution coefficient for a equilibrium concentration of  $5 \mu\text{g mL}^{-1}$

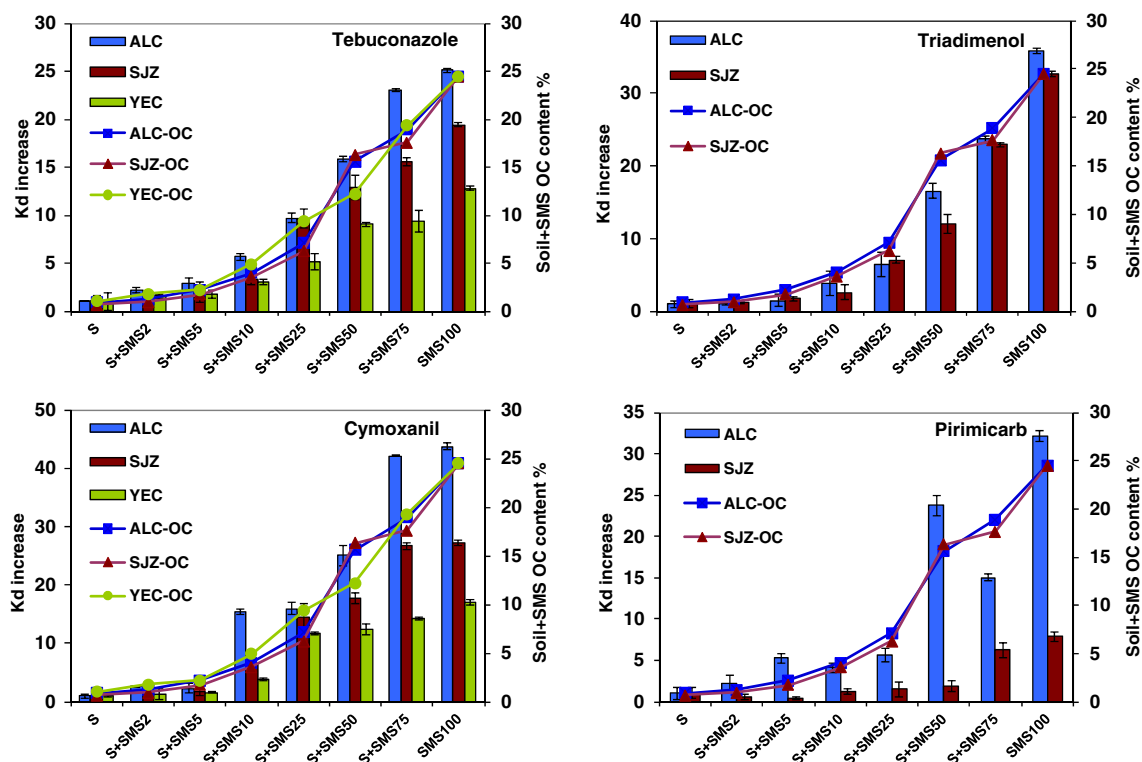
isotherms were different to 1.  $K_{d5}$  varied between 1.99 and 3.91 (tebuconazole) and between 1.36 and 1.50 (triadimenol) for unamended soils, and these values increased after amendment (Table 3). Increasing the SMS rates led to a constant increase in the adsorption efficiency for both pesticides. The higher adsorption of pesticides by ALC, SJZ, and YEC amended soils was somewhat similar and apparently depended only on the total OC content of the SMS-treated soils. In fact, the relative standard deviation (RSD) of  $K_{d5}$  values normalized to OC content ( $K_{OC}$ ) for amended soils varied between 19.7 and 28.7 % for tebuconazole, and between 23.9 and 25.1 % for triadimenol. This variability of  $K_{OC}$  values was lower than that usually found between the adsorption coefficients of pesticides for soils normalized to soil OC content (Papiernik et al. 2006), and ascribed to the different nature of soil OC.

However, it should be noted that the efficiency of SMS applied to increase adsorption was relative to the adsorption capacity of pesticides by the unamended soil. Figure 2 includes the increases in  $K_{d5}$  after amendment relative to unamended soil (i.e.,  $K_{d5}$  amended soil/ $K_{d5}$  unamended soil) for tebuconazole and triadimenol in the soils studied. The minor efficiency of SMS for the retention of these pesticides was seen in YEC soil for tebuconazole and in SJZ soil for triadimenol due to the greater adsorption of these pesticides by these unamended soils. The higher clay content of both soils or the presence of montmorillonite in YEC soil, a clay

mineral with a greater adsorption capacity (Sánchez-Martín et al. 2006; Báez et al. 2015), may explain the increased adsorption of pesticides by these soils and the lower global adsorption by the soil + SMS.

The results indicated that a further increase in  $K_{d5}$  by up to three to five times may be achieved for both compounds when an amendment rate  $\leq 10\%$  was applied to the soils, with the highest increase for the ALC soil with the lowest adsorption capacity. This rate corresponds to an application of  $\approx 25\text{--}30\text{ t C ha}^{-1}$ , which could equal an agronomic rate of SMS when this organic waste was used as an amendment. In this case, the adsorption of pesticides by the amendment applied could avoid the rapid leaching of these compounds or the diffuse contamination of waters by the pesticides when they reach the soils. However, a higher application of this organic residue could be used when the immobilization of pesticides was the objective for the prevention of water contamination from a point pollution source due to the management of these compounds. Increases in  $K_d$  of up to more than 20 times could then be achieved by applying an appropriate SMS rate to the amended soils.

The effect of SMS on the retention of tebuconazole and triadimenol was corroborated statistically as being due mainly to the OC content from SMS. A highly significant correlation coefficient was obtained between  $K_{d5}$  coefficients for tebuconazole and triadimenol jointly considered with the soil OC content ( $p < 0.001$ ). On the basis of the determination



**Fig. 2** Increases in adsorption distribution coefficients ( $K_d$ ) of non-polar and polar pesticides by amended soils at different SMS-rates and organic carbon (OC) of amended soils. Error bars represent the standard deviation of the mean value ( $n = 2$ )

coefficient  $r^2$ , the OC would account for 90.8 % of the variance in adsorption according to the equation  $K_d5 = 1.039 (\pm 1.137) + 1.923 (\pm 0.103) \text{OC}$ . The results were also subjected to a multiple linear regression analysis by combining two or more variables to determine the relative importance of soil parameters and/or pesticide parameters when they vary simultaneously. The inclusion of DOC and soil clay content in the multiple correlation model did not increase the variance in adsorption ( $R^2 = 89.8$ ). However, the inclusion of the  $K_{ow}$  of pesticides according to the positive correlation generally reported between the hydrophobicity of organic pollutants and adsorption (Nam et al. 2014) revealed a significant increase in the variance of adsorption, with the relationship between  $K_d5$  adsorption constants and the OC content and  $K_{ow}$  following the equation  $K_d5 = -39.65 (\pm 8.419) + 1.931 (\pm 0.081) \text{OC} + 11.65 (\pm 2.396) K_{ow}$ . The determination coefficient  $R^2 = 94.6$  % accounts for a higher percentage of  $K_d5$  variability than that explained when only the OC content is considered as the responsible variable. The equation obtained could be used to predict the adsorption of a non-polar pesticide from the increase in OC content by applying different rates of SMS to soil as a function of the purpose to be achieved.

**Effect of different rates of SMS on the adsorption of polar pesticides by soils**

The adsorption isotherms of cymoxanil and pirimicarb for unamended soils, SMS, and soils amended with doses of SMS in the 2–75 % range are included in Fig. 1. All the isotherms fitted the Freundlich equation with  $r$  values  $\geq 0.98$  and  $\geq 0.96$ , respectively.  $K_f$  and  $nf$  parameters were determined from the linear form of this equation (Table 4). All the adsorption isotherms of cymoxanil for unamended and amended soils were non-linear (L-type), with  $nf$  values in general  $< 0.90$ . No changes in linearity were observed for the isotherms of cymoxanil adsorbed by soils amended at different rates, as indicated for non-polar pesticides. Similar non-linear shapes were obtained for the adsorption isotherms of pirimicarb for unamended and amended soils, although the isotherms of this compound were S- or L-type, being unrelated to the SMS rate applied. Only adsorption mechanisms can explain the retention of these pesticides by SMS-soils, as reported for polar pesticides in general (Wang et al. 2011).

The  $K_f$  values for the adsorption of cymoxanil and pirimicarb were in the 0.29–0.58 and 0.44–0.78 ranges, respectively, for unamended soils, and 8.74 and 13.8, respectively, for SMS. The adsorption coefficients by soils and SMS are up to ten times and up to five times lower than those obtained for non-polar pesticides. The increase in soil OC content after SMS amendment enhanced the adsorption of both polar pesticides by amended soils (Table 4), and a significant correlation coefficient was also found between the  $K_f$

values and OC content of soils, although these  $r$  values were lower for polar pesticides than for non-polar pesticides. A positive correlation was also obtained between  $K_f$  and DOM for both pesticides although it was not always significant ( $r = 0.793–0.914$  ( $p < 0.1–0.05$ ) for cymoxanil and  $r = 0.683–0.936$  for pirimicarb ( $p > 0.10–< 0.01$ )). There could be interactions between DOC molecules from amendments and mineral soil surfaces competing with polar pesticide molecules for the same mineral adsorption sites.

To compare the sorption capacity of pesticides by soils amended with different rates of SMS, the  $K_d$  distribution coefficients were determined at an equilibrium concentration, because  $nf$  values were different to 1. An equilibrium concentration of  $40 \mu\text{g mL}^{-1}$  was selected from the wide range of concentrations considered for the adsorption isotherms.  $K_d40$  varied for unamended soils between 0.12 and 0.33 for cymoxanil and between 0.62 and 2.54 for pirimicarb (Table 4), and these values increased after amendment compared to the unamended soil. The effect of SMS on the retention of cymoxanil and pirimicarb increased with the OC content provided by the SMS, as indicated by non-polar pesticides. However, it was noted that the RSD of  $K_d40$  values normalized to OC content for amended soils fell within a wide range 23–44 % (cymoxanil) and 40–94 % (pirimicarb), indicating that other soil properties could also affect the adsorption of these pesticides by amended soils.

As seen for non-polar pesticides, the increases in  $K_d40$  for cymoxanil and pirimicarb in soils after amendment compared to unamended soils (Fig. 2) indicated a lower effect of the SMS for the retention of these pesticides in YEC and SJZ soil because of the greater adsorption of pesticides by these unamended soils. The effect of SMS to increase the adsorption of pirimicarb was very low in SJZ soil with a greater clay content, and this is consistent with reports in the literature on the adsorption of pirimicarb by clay minerals (Wei et al. 2001).

The results indicated that a further increase in  $K_d40$  of up to 15 times for cymoxanil and up to 5 times for pirimicarb may be achieved when a rate of amendment  $\leq 10$  % was applied, and higher increases in  $K_d40$  may be achieved in amended soils with doses of SMS  $> 25$  % for cymoxanil. Increases in the adsorption of pirimicarb were lower than cymoxanil, and in SJZ soil, they decreased after amendment at low rates compared to unamended soil, indicating that the SMS effect was not found for polar pesticides in all the soils.

A significant correlation coefficient was found between OC content and adsorption constants  $K_d40$  when the results of both pesticides were considered jointly, although the determination coefficient  $r^2$  was lower than that found for non-polar pesticides and accounted for 56.2 % of the variance in adsorption according to the equation  $K_d40 = 0.201 (0.721) + 0.441 (0.066) \text{OC}$ . This coefficient improved when DOC and clay content were included in the model ( $R^2 = 58.8$  %), and it accounted for up to 71.8 % of the variance in adsorption when



**Table 4** Freundlich adsorption constants and distribution coefficients of polar pesticides by soils amended at different SMS rates

Soil	Cymoxanil				Pirimicarb			
	$K_f \pm SD^a$	$nf \pm SD$	$K_d40^b \pm SD$	$K_{OC}$	$K_f \pm SD$	$nf \pm SD$	$K_d40 \pm SD$	$K_{OC}$
ALC	0.46±0.00	0.78±0.02	0.12±0.00	14.5	0.44±0.16	0.87±0.03	0.62±0.82	69.9
ALC+SMS2	0.82±0.12	0.75±0.01	0.33±0.02	27.0	2.29±0.10	1.11±0.03	1.41±0.01	116
ALC+SMS5	0.99±0.10	0.61±0.03	0.28±0.01	13.0	2.57±0.61	1.06±0.09	3.26±0.37	147
ALC+SMS10	3.65±0.14	0.83±0.01	1.98±0.30	49.6	3.46±0.10	0.92±0.03	2.56±0.22	64.1
ALC+SMS25	4.39±0.43	0.79±0.03	2.05±0.36	28.9	5.11±0.27	0.89±0.05	3.49±0.09	49.2
ALC+SMS50	5.21±0.34	0.87±0.03	3.23±0.07	20.7	18.1±0.33	0.95±0.04	14.8±0.30	94.8
ALC+SMS75	6.23±2.08	0.96±0.11	5.42±0.53	28.7	19.6±0.13	0.82±0.00	9.35±2.86	49.5
SJZ	0.29±0.00	0.78±0.02	0.21±0.02	31.0	0.78±0.10	1.32±0.05	2.54±0.11	379
SJZ+SMS2	0.49±0.01	0.86±0.07	0.30±0.01	30.8	1.18±0.22	0.86±0.02	1.39±0.10	143
SJZ+SMS5	0.81±0.20	0.79±0.11	0.37±0.12	21.3	2.33±0.03	0.81±0.01	1.08±0.08	62.9
SJZ+SMS10	1.48±0.05	0.96±0.01	1.30±0.11	36.5	5.82±0.03	0.83±0.01	3.16±0.68	88.8
SJZ+SMS25	5.24±0.17	0.85±0.01	2.99±0.01	47.9	6.59±0.76	1.01±0.04	3.88±0.31	62.1
SJZ+SMS50	6.79±0.07	0.83±0.00	3.68±0.10	22.6	7.94±0.04	0.86±0.00	4.73±0.08	29.1
SJZ+SMS75	8.26±0.04	0.89±0.00	5.54±0.12	31.5	12.1±0.47	1.07±0.02	15.9±0.13	90.3
YEC	0.58±0.02	0.82±0.01	0.33±0.05	33.1				
YEC+SMS2	1.01±0.14	0.77±0.01	0.43±0.09	24.4				
YEC+SMS5	1.19±0.02	0.78±0.05	0.52±0.07	23.7				
YEC+SMS10	2.81±0.08	0.79±0.01	1.27±0.01	26.0				
YEC+SMS25	6.89±0.21	0.84±0.00	3.84±0.07	41.2				
YEC+SMS50	6.33±0.17	0.88±0.01	4.08±0.11	33.5				
YEC+SMS75	9.77±0.02	0.81±0.00	4.72±0.27	24.5				
SMS	8.74±0.05	0.88±0.01	5.64±0.02	23.0	13.8±0.17	1.11±0.02	20.0±0.59	81.7

<sup>a</sup> SD, standard deviation ( $n=2$ )

<sup>b</sup> Distribution coefficient for a equilibrium concentration of 40  $\mu\text{g mL}^{-1}$

the OC, DOM, clay, and  $K_{ow}$  variables were considered according to the equation  $K_d40 = -2.713 (1.448) + 0.224 (0.122) OC + 3.707 (2.313) DOC + 0.008 (0.042) \text{clay} + 2.757 (0.740) K_{ow}$ . The adsorption of a polar pesticide was not fully predicted from the increase in OC content by applying different rates of SMS to the soil, as it was for non-polar pesticides. However, the increased adsorption of these hydrophilic pollutants by SMS in amended soils was important despite their lower hydrophobicities, as indicated for other hydrophilic micropollutants adsorbed by organic materials (Nam et al. 2014).

#### Estimation and possible prediction of adsorption coefficients of non-polar and polar pesticides for SMS amended soils

A comparison between estimated and experimental adsorption coefficients  $K_d$  for the non-polar pesticides tebuconazole and triadimenol and the polar pesticides cymoxanil and pirimicarb for SMS-amended soils was carried out in order to know whether it is possible to predict the  $K_d$  adsorption values of pesticides for SMS-amended soils. The  $K_d$  values for soils

amended with different rates of SMS were estimated from the  $K_d$  coefficients obtained by individual components (soil and SMS), as some reports have indicated in the literature (Wang et al. 2010; Chen and Yuan 2011) from the equation  $K_d = f_{SMS} K_{dSMS} + f_{soil} K_{dsoil}$ , where  $f_{SMS}$  and  $f_{soil}$  are the fractions of SMS and soil for different rates of SMS applied to soils in the different soil-SMS mixtures, and  $K_{dSMS}$  and  $K_{dsoil}$  are the adsorption distribution coefficients of pesticides for each individual SMS and soil. Linear regressions were then obtained between the  $K_d$  estimated and the experimental values for the different pesticides and amended soils assayed.

The results obtained included in Fig. 3 showed a significant correlation between both series of values (estimated and experimental) for non-polar pesticides;  $r$  ranged between 0.963 and 0.998 ( $p < 0.01$ ) for tebuconazole and between 0.989 and 0.996 ( $p < 0.01$ ) for triadimenol. Accordingly, these estimated values could be used for predicting the adsorption of these compounds by soils after SMS amendment at different rates from the adsorption data of pesticides by the unamended soil and by SMS. Therefore, the adsorption of non-polar pesticides could be optimized using SMS as a tool to adjust soil adsorption depending on the purpose to be achieved.

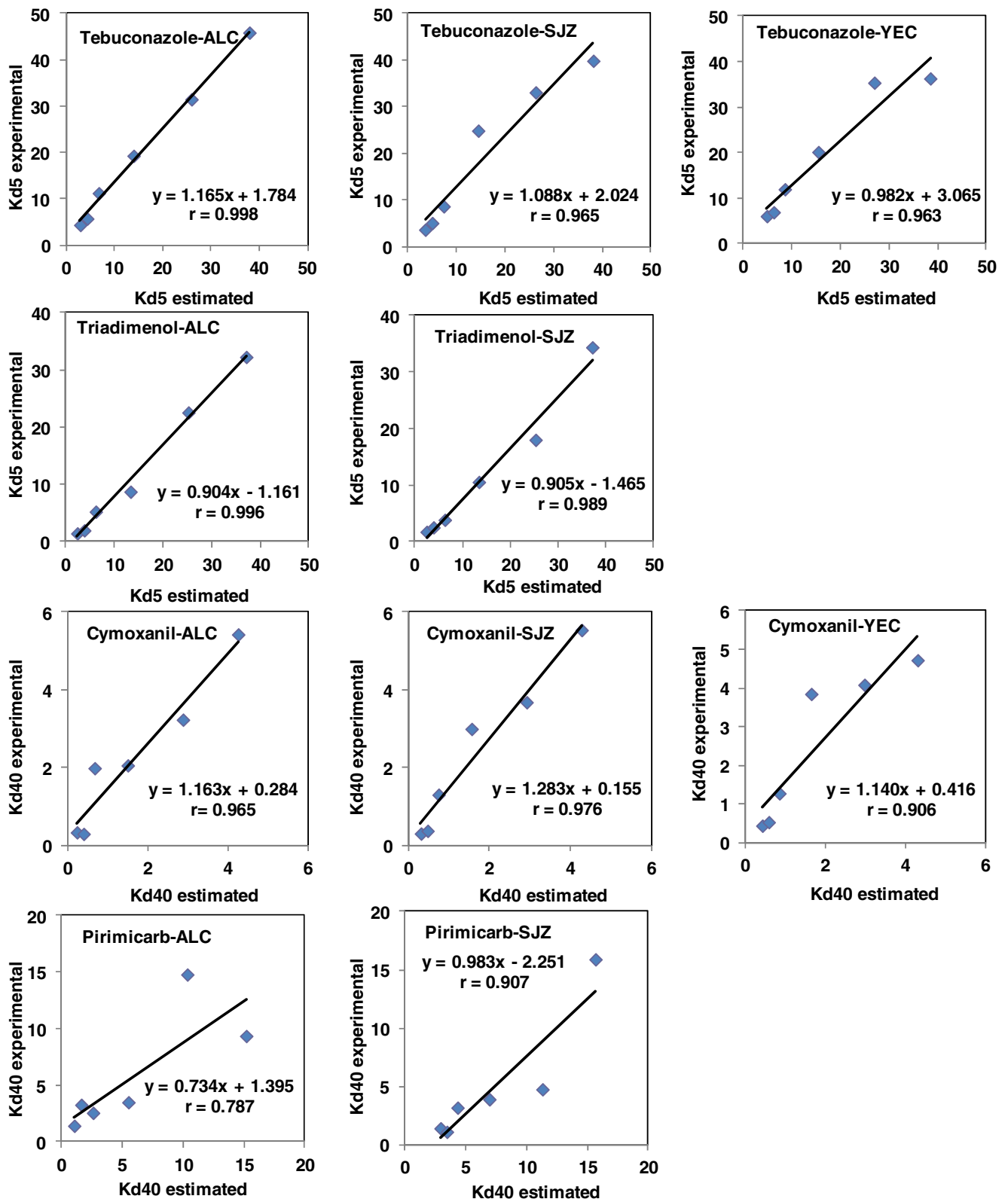


Fig. 3 Linear regressions between estimated and experimental  $K_d$  adsorption coefficients of non-polar and polar pesticides by SMS-amended soils

However, the correlation coefficients obtained for linear regressions between the estimated and experimental values obtained for polar pesticides (Fig. 3) were lower than those

obtained for non-polar pesticides;  $r$  ranged between 0.906 and 0.976 ( $p < 0.05$ ) for cymoxanil, and between 0.787 and 0.907 ( $p < 0.1$ ) for pirimicarb. The results indicated a poor match

between estimated and experimental adsorption values. The adsorption values estimated from the equations were increased or decreased for cymoxanil and pirimicarb compared to the experimental adsorption values. Different adsorption mechanisms for the retention of non-polar or polar pesticides and amended soils could explain these results.

## Conclusions

Adsorption of non-polar and polar pesticides by SMS-amended soils increased due to the increase in OC provided by the biosorbent SMS.  $K_d$  values increased (i) 3 to 5 times for tebuconazole and triadimenol and 5 to 15 times for pirimicarb and cymoxanil for SMS rates  $\leq 10\%$  (similar to the agronomic rate) and (ii) more than 20 times for non-polar and polar pesticides by applying SMS to soils at rates  $\geq 25\%$ . The OC content of SMS-soils accounted for more than 90 % of the variability in the adsorption of non-polar pesticides, but it accounted for only 56.2 % for polar pesticides, indicating the influence of other soil parameters in the adsorption of these polar pesticides. Estimated adsorption results for soils and SMS were consistent with experimental data mainly for non-polar pesticides and could be used for predicting the adsorption of these compounds by SMS-soils. The results indicate the possibility of using the low-cost biosorbent SMS as a tool for optimizing the adsorption capacities of pesticides by agricultural soils in order to apply the most appropriate biosorbent rates to prevent diffuse or point contamination, and avoid the leaching of pesticides into groundwater.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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