JOURNAL OF SOILS AND SEDIMENTS (2012) 12: 1111-1123

SOILS, SEC 4 • ECOTOXICOLOGY • RESEARH ARTICLE

Changes in the sorption-desorption of fungicides over time in an amended sandy clay loam soil under laboratory conditions

Jesús M. Marín-Benito • M. Soledad Andrades • M. Sonia Rodríguez-Cruz • María J. Sánchez-Martín

J. M. Marín-Benito • M. S. Rodríguez-Cruz • M. J. Sánchez-Martín (✉)
Instituto de Recursos Naturales y Agrobiología de Salamanca (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, Spain
e-mail: mjesus.sanchez@irnasa.csic.es

M. S. Andrades
Departamento de Agricultura y Alimentación, Universidad de La Rioja, Madre de Dios 51, 26006 Logroño, Spain

(✉) **Corresponding author:**
Phone: 34 923 219606
Fax: 34 923 219609
e-mail: mjesus.sanchez@irnasa.csic.es

Abstract

Purpose: The aim of this work was to study the temporal changes in the sorption-desorption of fungicides in a sandy clay loam soil amended with spent mushroom substrate (SMS) under controlled laboratory conditions and the influence that fungicides properties and soil characteristics have on these processes. Soil amendment with SMS is becoming a widespread management practice since it can effectively solve the problems of uncontrolled SMS accumulation and disposal and improve soil quality. However, when simultaneously applied with pesticides, SMS can significantly modify the environmental behaviour of these compounds.

Materials and methods: Sorption-desorption isotherms of metalaxyl, penconazole, pyrimethanil and iprovalicarb for an unamended and amended vineyard soil from La Rioja (Spain) were obtained. Composted SMS (C-SMS) and fresh SMS (F-SMS) from cultivation of different mushrooms were used as amendments at 2% and 10% rates. Soil parameters (organic carbon (OC), dissolved organic carbon (DOC), humic acid (HA) and fulvic acid (FA)) and sorption (Kf, nf, Kd, Koc) and desorption (Kfd, nfd, H) parameters of fungicides were determined over 0, 6 and 12 months of soil incubation with SMS under controlled conditions.

Results and discussion: Addition of amendments to soil increased soil sorption capacity of fungicides. Kd values increased with the hydrophobic character of fungicides (metalaxyl < iprovalicarb < pyrimethanil < penconazole) at both amendment rates. The lower content of DOC and the higher degree of OC humification enhanced sorption of all fungicides by the soil+C-SMS with regard to the soil+F-SMS. In general, sorption of fungicides decreased after 6 and 12 months of soil+SMS incubation, although the humification degree of the remaining OC expressed by HA/FA increased. This might indicate that the OC content was more important for fungicide sorption than the changes in its nature with the incubation time. SMS addition favoured desorption of metalaxyl and iprovalicarb, in general, whereas irreversible sorption of penconazole and pyrimethanil increased. However, the opposite trends were observed when the soil+SMS incubation time increased.

Conclusions: The results show an increase in sorption of all fungicides by amending soil with composted or fresh SMS. However, desorption of fungicides increases or decreases depending on the properties of fungicides and soil+SMS. Changes in both processes with the incubation time are more related to the OC content of the amended soil than to the evolution of its nature. These outcomes are of interest for extending SMS application to soil with minimal or no environmental risk when used simultaneously with fungicides.

Keywords Desorption • Fungicides • Soil • Soil incubation • Sorption • Spent mushroom substrate

1 Introduction

The application of organic residues to soil is nowadays an increasingly common agricultural practice due to the environmental problems caused by the uncontrolled accumulation and disposal of such residues and to the well-known benefits for soil fertility in terms of organic matter (OM) and nutrient soil enrichment (García-Izquierdo and Lobo 2008). This practice is also a way to sequester carbon and reduce greenhouse gas emissions (Spokas et al. 2009; Zhang et al. 2012). The organic residues potentially applicable to soil come from household activities (sewage sludge or urban solid waste) and agriculture (crop residues, wine or olive oil production or mushroom cultivation). In recent years, the accumulation of spent mushroom substrate (SMS) has significantly risen due to increased mushroom production in China, USA, France, the Netherlands and Spain (FAOSTAT 2009). Some studies have reported an appropriate use of SMS for different purposes (Wuest et al. 1995), but its use as a soil amendment in a raw or composted state has been the most effective due to the high load of OM and low charge of toxic elements (Chiu et al. 2000).

In Spain, mushrooms are grown extensively in the La Rioja region, and SMS is often used as a vineyard soil amendment. Due to intensive vine cultivation, the local soils have been seriously degraded and require ameliorating through soil management activities (Miguéns et al. 2007). However, the OM of these residues may interfere with the dynamics of the pesticides (mainly fungicides) used in the vineyards. Fungicides are widely used to control vine fungal diseases, and their use has increased sharply over the past few years in step with greater vine cultivation. Fungicides reach the amended soil either by direct application to the soil or by the subsequent wash-off from treated plants, and interaction with the OM of the residues can increase or decrease its sorption with respect to the unamended soil (Briceño et al. 2007; de Wilde et al. 2009).

The effect of natural soil OM on the environmental behaviour of pesticides has been described (Clapp et al. 2001). However, the nature and composition of the OM of organic residues is so variable that it is practically impossible to predict its effect on the environmental behaviour of pesticides. Of special interest is the sorption-desorption of pesticides by soils and how such processes can be affected by the practice of soil amended with organic residues (Reichenberger et al. 2007, Arias-Estévez et al. 2008). This could have important implications for the harmful presence of pesticides in surface and ground water due to sustained leachability or run-off processes (Fenoll et al. 2011; Rodriguez-Cruz et al. 2011).

The literature has often investigated the effect of soil application of different organic residues, such as sewage sludge, urban, winery and olive wastes, and pig or cow manure, on the behaviour of herbicides (Delgado-Moreno 2007, Briceño et al. 2008, Wang et al. 2010, López-Piñeiro et al. 2011), insecticides (Sánchez-Camazano et al. 1997, Sánchez et al. 2003) and fungicides (Fernandes et al. 2006, Ghosh and Singh 2009, Filipe et al. 2010). The results from these studies highlight the importance of the kind and nature of the residue, its manipulation and processing, and the rate of its application to the soil. These studies are normally carried out with soils amended under laboratory conditions or over short incubation times, normally of 1-60 days. Only rarely are studies conducted over longer times, when the OM load of soil decays naturally by mineralization at ambient conditions and evolves to a more stable form by humification.

Our group has recently initiated a research project designed to clarify some of these unexplored aspects regarding SMS addition to soil as an amendment. Field experiments with plots amended with SMS from *Agaricus bisporus* cultivation have been performed to evaluate the sorption and mobility parameters of penconazole and metalaxyl by soils and subsoils (Marín-Benito et al. 2009a, b) or the dissipation and persistence parameters of tebuconazole in soil (Herrero-Hernández et al. 2011). The results reveal changes in these processes which modify the behaviour of these fungicides at the beginning of the incubation period with a consequent more probable impact onto the contamination of waters.

Accordingly, and with a view to establishing a sound practice for the use of SMS as an amendment in soils, the objectives of this work were as follows: 1) evaluate the changes in the sorption-desorption features of four fungicides of different chemical class used in vineyards, using an SMS-amended sandy clay loam soil over 0, 6 and 12 months of incubation under laboratory conditions; 2) study the effect onto sorption-desorption processes of the application rate of SMS, of the kind of treatment, composted and fresh state, and of the properties of the used SMS and fungicides.

2 Materials and methods

2.1 Fungicides

Selected characteristics of the fungicides studied are included in Table 1 (Tomlin 2000, FOOTPRINT 2011). Fungicides are solid and belong to different chemical classes. Penconazole (triazole) and metalaxyl (acetylalaninate) were supplied by Novartis Crop Protection AG (Basel, Switzerland). They were used unlabeled (purity ≥ 98%) and ^{14}C-labeled with specific activity and purity of 1.02 MBq mg^{-1} and >98% for ^{14}C-penconazole and 1.37 MBq mg^{-1} and >97.2 for ^{14}C-metalaxyl. Pyrimethanil (pyrimidinamine) and iprovalicarb (carbamate) were supplied by Riëdel de Haën (Hannover, Germany) (> 97.5% purity).

2.2 Spent mushroom substrates

Two SMSs supplied by INTRAVAL (La Rioja, Spain) were used as soil amendments. The composted SMS (C-SMS) is a commercial SMS (Intracompost SPCH-SPS) from *Agaricus bisporus* (75%) and *Pleurotus spp*. (25%) production. This C-SMS is obtained by composting the substrate removed from the mushroom houses in piles (2.5 m high) for several weeks under aerobic conditions. The fresh SMS (F-SMS), from *Lentinula edodes* or Shiitake production, was obtained immediately after being removed from the mushroom houses and used without composting. The SMS samples were dried at 45ºC, ground and sieved (< 1 mm) on arrival and stored at room temperature for later use. Their characteristics are shown in Table 2. The pH was determined in SMS/water suspensions (1/2 w/v ratio), ash was determined by loss on ignition at 540ºC and OM was calculated as 100 - % ash. The organic carbon (OC) content was determined by dichromate oxidation (Walkley-Black method) (Nelson and Sommers, 1996). The dissolved organic carbon (DOC) was determined in a suspension of SMS in Milli-Q ultrapure water (1/100 w/v ratio) after shaking (24 h) at 20ºC, centrifugation (20 min at 12,800 g), and filtering through a 0.45 µm filter (Millex HV_{47} Millipore) using a Shimadzu 5050 carbon analyzer (Shimadzu, Columbia, MD, USA). All the determinations were carried out in triplicate. Total N was determined by the Kjeldahl method

(Bremner 1996). Metals (Cd, Cr, Cu, Ni, Pb, Zn and Hg) were determined as indicated in Marin-Benito et al. (2009a).

2.3 Unamended and amended soils

The soil sample was taken from the surface horizon (0-30 cm) in a vineyard in the La Rioja region, specifically located in Aldeanueva (Al) (42º14’0”N latitude and 1º53’0”W longitude). It was air-dried and sieved (< 2 mm), and the soil characteristics were determined by standard analytical methods (MAPA, 1986). Aldeanueva soil is a Fluventic Haplocambids (Soil Survey Staff 2006) and its texture was classified as sandy clay loam. The particle size distribution determined using the pipette method was 64.4% sand, 14.2% silt and 21.4% clay, and the inorganic carbon, determined as $CaCO_3$ with a Bernard calcimeter, was 11.3%. The pH determined in a soil/water suspension (1/1 w/v ratio) was 7.8 and the OC determined as indicated above for SMS was 0.59. DOC was determined in soil/Milli-Q ultrapure water extracts (1/2 w/v ratio) as previously indicated. In addition, alkali soluble and acid insoluble carbon (humic acid, HA) and alkali and acid soluble carbon (fulvic acid, FA) were also obtained in soil extracts following the traditional method of HA and FA extraction from soil OC (Stevenson 1982).

Amended soil specimens were prepared by uniformly mixing Al soil with commercial composted SMS (Al+C-SMS) or with Shiitake fresh SMS (Al+F-SMS) at rates of 2% and 10%, respectively, on a dry weight basis (equivalent to ~25 and ~125 t SMS ha^{-1} considering a soil depth of ~10 cm and a soil density of ~1.3 g cm^{-3}). The initial moisture content of the soils was adjusted to 40% of their maximum water holding capacity. Unamended and amended soils (~200 g) were then incubated in beakers at 20±2ºC in the dark during 0, 6 and 12 months. The soil moisture was kept constant during the entire period of the experiment.

The characteristics of the soils incubated for different lengths of time were determined as indicated for the unamended soil (Table 3).

2.4 Sorption experiments

The sorption-desorption isotherms of fungicides for air-dried unamended soils and soils amended with SMS after 0, 6 and 12 months of incubation were obtained using the batch equilibrium technique. Duplicate samples of the soils (5 g) were equilibrated with 10 mL of a Milli-Q ultrapure water solution of each fungicide at concentrations of 1, 5, 10, 15, 20 and 25 μg mL^{-1} for penconazole, pyrimethanil and metalaxyl and 0.5, 1, 2, 3, 4 and 5 μg mL^{-1} for iprovalicarb. An activity of 100 Bq mL^{-1} was used for ^{14}C-penconazole and ^{14}C-metalaxyl. The suspensions were shaken at 20±2ºC for 24 h in a thermostated chamber, with intermittent shaking for 2 h at three-hour intervals. Preliminary experiments revealed that contact for 24 h was long enough for attaining equilibrium. The suspensions were subsequently centrifuged at 5045 g for 15-30 min, and the supernatant was filtered through a 0.45 μm filter (Millex HV_{47} Millipore). The equilibrium concentrations of the fungicides in the supernatant were then determined by liquid scintillation counting or high-performance liquid chromatography (HPLC)/mass spectrometry (MS) as indicated in section 2.5. The amount of fungicide sorbed was the difference between that initially present in solution and that remaining after equilibration with the soil.

The desorption isotherms of the fungicides were obtained from samples initially treated with 25 μg mL^{-1} of penconazole, pyrimethanil and metalaxyl solution or 5 μg mL^{-1} of iprovalicarb solution. After the samples had been shaken and centrifuged as indicated for the sorption, 5 mL of supernatant was immediately replaced by 5 mL of ultrapure water. The resuspended samples were shaken at 20±2ºC for 24 h, after which they were centrifuged and the amount of fungicide desorbed was measured. This desorption procedure was repeated four times for each sample. The amount of fungicide sorbed by the soils at each desorption stage was calculated as the difference between the initial amount sorbed and the amount desorbed.

2.5 Fungicide analysis

The quantitative determination of ^{14}C-penconazole and ^{14}C-metalaxyl after sorption was made on a Beckman LS6500 liquid scintillation counter (Beckman Instruments Inc., Fullerton, CA). The radioactivity of the equilibrium solution was measured in disintegrations per minute (dpm), being determined in 1 mL of supernatant to which 4 mL of scintillation cocktail had been added. The dpm value recorded was related to the dpm obtained for aliquots of the respective standards of the fungicide solutions. These determinations were carried out in duplicate for all the solutions, and the coefficient of variation was always < 2%.

Pyrimethanil and iprovalicarb were quantified by HPLC with diode array (DAD) and mass spectrometer (MS) detectors (Waters Association, Milford, MA), using a Waters Symmetry C18 column (75 x 4.6 mm inner diameter, 3.5 μm) at ambient temperature. The mobile phase was 80/20 (v/v) methanol/water (0.1% formic acid) for pyrimethanil, and 60/40 acetonitrile/water (0.1% formic acid) for iprovalicarb. The flow rate of the mobile phase was 0.3 mL min^{-1} and the sample injection volume was 20 μL. Calibration curves were generated from 0.05-2.0 μg mL^{-1} (pyrimethanil) and 0.125-2.0 μg mL^{-1} (iprovalicarb) concentrations of standards in solutions of sorbent extracts to counteract any possible matrix effect. Retention time was 6.0 and 7.1 min for pyrimethanil and iprovalicarb, respectively, and the limits of detection (LOD) and quantification (LOQ) were, respectively, 0.54 and 1.78 μg L^{-1} for pyrimethanil determination and 0.69 and 2.27 μg L^{-1} for iprovalicarb determination. Quantitative analysis was performed using the peak area of each compound obtained from the total ion chromatogram (TIC) in SIM mode. The positive molecular ion (m/z) was 200.18 and 321.30, for pyrimethanil and iprovalicarb, respectively.

2.6 Data analysis

The sorption data of the fungicides were fitted to the linearised form of the Freundlich equation: log Cs = log Kf + nf log Ce, where Cs (μg g^{-1}) is the amount of sorbed fungicide; Ce (μg mL^{-1}) is the equilibrium concentration of fungicide in solution, and Kf (μg^{1-nf} g^{-1} mL^{nf}) and nf are the Freundlich sorption and non-linearity coefficients, respectively. Kd (mL g^{-1}) distribution coefficients were also determined from the relationship between Cs and Ce, for a Ce of 5 μg mL^{-1} for metalaxyl, penconazole and pyrimethanil and 2 μg mL^{-1} for iprovalicarb because of the non-linearity of isotherms. Kf values normalised to 100% OC (Koc) were calculated as Kd 100/%OC. Standard deviation (SD) was used to indicate variability in the sorption coefficients among replicates. Sorption constants values were subjected to an analysis of variance, and the least significant difference (LSD), at a confidence level of 95%, was determined to measure the effects of different treatments on the sorption of fungicides by soils.

3 Results and discussion

3.1 Sorption of fungicides by non-incubated soil

The sorption isotherms of fungicides for Al soil amended with SMS at rates of 2% and 10% immediately after its incorporation in soil (T 0m) and in unamended soil are reported in Fig. 1. Isotherms are generally L-type (non-linear) and resemble a C-type, indicating that different mechanisms of sorption may exist between fungicides and soil components and/or residue moieties (Chiou et al. 2000). This kind of isotherm has frequently been found in the sorption of other pesticides that are not extremely hydrophobic, such as triazines, organophosphates, phenylureas, or compounds with chemical groups similar to those of the fungicides considered (Wauchope et al. 2002).

The sorption isotherms fit the Freundlich equation, $r \geq 0.98$ ($p < 0.01$), and the Kf and nf parameters were determined from the linear form of this equation. The nf values were 0.89 (metalaxyl), 0.83 (penconazole), 0.74 (pyrimethanil) and 0.95 (iprovalicarb) in the case of the unamended soil, and a slight increase was observed when soil was amended with both rates of SMS.

The Kf sorption constants of the fungicides by the unamended soil varied from 0.24 to 5.17, increasing in the following order: metalaxyl < iprovalicarb < pyrimethanil < penconazole, according to the Kow values of the fungicides, except in the case of iprovalicarb. A similar sorption pathway was observed for SMS-amended soils (Table 4); that is, sorption increased as the hydrophobic nature of the fungicide rose. The Kd distribution coefficients were determined to compare the sorption capacity of fungicides by soil because nf values were different to 1. They varied between 0.20 and 3.95 for the unamended soil (Table 5), and a significant increase was also observed when SMS was added (LSD = 0.012, $p < 0.001$ for metalaxyl, LSD = 0.74, $p < 0.001$ for penconazole, LSD = 1.19, $p < 0.001$ for pyrimethanil and LSD = 0.33, $p < 0.01$ for iprovalicarb) especially at the higher rate (10%). The Kd constant for the non-incubated soil (time zero, T 0m) amended with C-SMS increased by 2.45-6.50 times for metalaxyl, 2.47-6.71 times for penconazole, 2.61-8.82 times for pyrimethanil and 1.14-4.52 times for iprovalicarb. When the soil was amended with F-SMS, the increase of the constant was lower: 1.25-3.50 times for metalaxyl, 1.73-3.85 times for penconazole, 1.72-6.15 times for pyrimethanil and up to 3.23 times for iprovalicarb. This seemed to contrast with the observed higher OC content of the Al+F-SMS mixing (see Table 3). As reported by previous unpublished studies (Marin-Benito, 2011), the OC content should favour fungicide sorption, as revealed by the positive and significant correlation ($r \geq 0.94$, $p < 0.001$) between Kd coefficients and the OC of unamended vineyard soils with OC < 2%. Thus, the greater sorption capacity of the Al+C-SMS soil could be explained by the higher degree of humification of the OC expressed by the elevated value of the ratio HA/FA and/or by the lower content of DOC (see Table 3) relative to the Al+F-SMS soil. These characteristics of the amended soil are related to the main features of the residues applied, C-SMS and F-SMS (see Table 2).

The increase in the sorption of the organic compounds by soils due to the rise in the degree of humification of the OM has often been reported in the literature (Ahmad et al. 2001). The effects that DOC has on the sorption of pesticides and hydrophobic compounds by soils are contradictory. Some authors (Barriuso et al. 1992; Andrades et al. 2004) report an increase in the sorption of pesticides if organic soluble compounds from DOC are sorbed by soils and give rise to the formation of new hydrophobic surfaces. A decrease in sorption might occur if pesticides interact with the soluble moieties of OM in the soil-solution interface (Müller et al. 2007, Luo et al. 2009) or when the pesticides compete with the soluble organic molecules for the same sorption sites (Briceño et al. 2008, Cox et al. 2007). These effects could explain our results, which indicated decreased fungicide sorption by the amended soil mixtures with the highest DOC load. Likewise, a significant multiple correlation was found for each fungicide between the Kd and the OC and DOC contents of soil mixtures. This correlation evidenced the contrasting effects of the OC and DOC loads of the amended soil on fungicide sorption, as determined by the batch equilibrium technique. The determination coefficients R^2 of the multiple correlation indicated that more than 90% of the variability of the sorption could be explained by the OC and DOC contents for all the fungicides (penconazole > pyrimethanil > metalaxyl > iprovalicarb) (Table 6).

3.2 Sorption of fungicides by incubated soil

Fig. 1 shows the sorption isotherms of the fungicides for the unamended and amended soil at the rates of 2% and 10% after 6 (T 6m) and 12 (T 12m) months of soil+residue incubation. The Freundlich parameters Kf and nf (see Table 4) and the Kd coefficients (see Table 5) of the fungicides were determined along with the changes in pH, OC, DOC, HA and FA with soil+SMS incubation time (see Table 3). In the case of the soil Al+C-SMS incubated over 12 months, a significant decrease ($p<0.01$) in OC up to 18% and in DOC up to 59% was observed, while in the case of the soil Al+F-SMS, the decrease was up to 55% for OC and up to 93% for DOC. For the soil Al+F-SMS, the pH increased in parallel with the sharp decrease observed in the OC load to a value close to the pH of the unamended soil. This trend was expected considering the low pH value of the F-SMS material close to 4.5. However, the composition of the remaining OC changed over time. The HA/FA ratio, which is an indicator of the degree of humification of the OC of the Al+C-SMS and Al+F-SMS soils, increased by 1.1-1.3 times and 1.5-2.6 times, respectively. The significant changes observed in the OC and DOC values appeared to be more significant within the first six months of incubation and then levelled off by 12 months of ageing.

The nf values of the sorption isotherms over time varied in a similar way for both unamended and amended soil, keeping close to values < 1. The Kd values followed the same variation pathway as those recorded at T 0m. With time, the Kd values did not significantly change for the unamended soil, whereas Kd decreased in the amended soils. The Kd values of penconazole significantly decreased up to 1.55-1.61 times after 6 and 12 months of incubation. The values of metalaxyl decreased up to 1.46 times, and of pyrimethanil up to 1.82-2.24 times, although the Kd decrease was not significant for soils treated with the lowest rate of SMS (2%) (Al+C-SMS2 and Al+F-SMS2), which had a lower OC content < 1.5%. The changes in the Kd values for iprovalicarb were quite irregular, decreasing in some cases up to 2.62-2.53 times, and increasing in others (see Table 5).

For all fungicides, the greater decrease in Kd corresponded to the soil amended with the fresh residue at a rate of 10% (Al+F-SMS10), which is also the soil-SMS combination with a more consistent decrease in the OC load. This mixture also recorded a very significant increase by up to threefold in the degree of humification of OC (see Table 3). The sorption of the fungicides studied appeared to be linked more closely to the decrease in the OC load of the amended soil than to the changes in the nature or structure of OC. Consistent with these findings, we found a significant linear regression between the Kd and the OC contents of the soil for all the fungicides studied, with correlation coefficient (r) values between 0.91-0.97 ($p < 0.05$) for soil incubated for six months (T 6m) and 0.88-0.99 ($p < 0.05$) for soil incubated for 12 months (T 12m). However, the latter changes after 12 months of incubation were also consistent with a significant correlation between Kd and the HA/FA ratio of the soil ($r > 0.97$, $p < 0.05$ for metalaxyl; $r > 0.95$, $p < 0.05$ for penconazole, $r > 0.97$, $p < 0.05$ for pyrimethanil and $r > 0.96$, $p < 0.05$ for iprovalicarb).

Likewise, other authors have reported a decrease in the sorption of triazines and diuron in soils amended with residues from the olive-mill or wine industries over a short time span (1.5-3 months) (Delgado-Moreno et al. 2007, Fernández-Bayo et al. 2009) even though the OC load remained practically unchanged. Other factors, such as the type of soil and the nature of the DOC added with the organic residue, were also proposed by Cox et al. (2004), and Fernandes et al. (2006) to explain the increase or decrease in the sorption of metalaxyl by soils incubated for two months with different types of amendments.

The sorption coefficients were normalised regarding the OC content (Koc) of the soil-SMS mixtures to evaluate the effect on sorption of different characteristics or types of OC. Mean Koc values and their relative coefficients of variation (CV) were obtained to evaluate the Koc variability of fungicides over time (see Table 5). The Koc values recorded a CV in the 24-51% range for the unamended and amended soils at T 0m, revealing the influence the nature of the OC of the residues has on the sorption of fungicides. Koc variability decreased with incubation time and CV varied in the 9.1-18.1% range for the sorption of metalaxyl, penconazole and pyrimethanil (fungicides with Kow values of 1.75-3.72). This highlighted the importance of the OC load after its evolution/stabilization process within the 12-month incubation of soils, rather than the OC nature of the amended soil, which was quite similar after this time. Iprovalicarb (Kow = 3.20) was an exception with a CV of 39.8-53.6%. Even though this fungicide has a slightly hydrophobic character, other soil factors besides OC might influence the sorption of iprovalicarb by the amended soils, as also reported by Sheng et al. (2001) for other carbamates.

3.3 Desorption of fungicides after 0, 6 and 12 months of incubation

The reversibility of fungicides sorbed by amended soils was studied by desorption isotherms from samples initially treated with 25 μg mL^{-1} of penconazole, pyrimethanil and metalaxyl solution or 5 μg mL^{-1} of iprovalicarb solution after 0, 6 and 12 months of soil+residue incubation (see Fig. 1). Kfd and nfd desorption parameters (Table 7) were obtained from the Freundlich equation ($r \geq 0.87$, $p < 0.01$) and hysteresis coefficients (H) were determined (H = nf/nfd) (Table 8). Desorption isotherms showed hysteresis, as the desorption data did not match those of the sorption isotherm, and the hysteresis coefficients obtained were constantly > 1 for both unamended and amended soils, indicating that the desorption process was not fully reversible.

For the unamended soil, the values of H were in the 1.10-10.1 range, with peak values observed for metalaxyl and iprovalicarb. The values of H for the desorption of penconazole (2.66-8.18) and pyrimethanil (1.51-4.40) were higher for the amended soil than for the unamended one, especially in the case of the soil Al+C-SMS at the higher SMS rate. However, the hysteresis of the desorption isotherms of metalaxyl (1.44-2.93) and iprovalicarb (1.32-4.39) from the amended soils was similar or decreased with respect to the unamended soil. The irreversibility of sorption of these fungicides decreased with the increase in the SMS rate, indicating that the organic residue facilitated the compound's desorption. After six months of incubation, a significant decrease in H was observed for penconazole, with an increase for pyrimethanil regarding the values at T 0m. After 12 months, an increase in H for metalaxyl and iprovalicarb and a decrease for pyrimethanil were recorded, whereas no significant changes were observed for penconazole as regards the values at T 6 m.

The amounts of each fungicide desorbed from unamended and amended soils after four consecutive desorption cycles and over the three different times of incubation are shown in Fig. 2. They are reported as percentages of fungicides with respect to the initial amounts sorbed, varying in the 41.8-75.8% range for metalaxyl, 34.9-35.9% for penconazole, 48.5-69.1% for pyrimethanil and 17.0-24.5% for iprovalicarb from the unamended soil, and in the 51.4-76.0% range for metalaxyl, 6.99-29.1% for penconazole, 15.8-57.6% for pyrimethanil and 30.5-79.4% for iprovalicarb from the amended soils.

The data reveal that the increase in OC due to the application of the organic residues led to a decrease in the desorption of penconazole and pyrimethanil from the amended soil with both rates of residues, although the effect was greater for the soil amended with C-SMS at a rate of 10%. The decrease in soil OC content after incubation caused a constant increase in penconazole desorption from the amended soil, and a variable effect on the pyrimethanil desorption was reported. The desorption of metalaxyl from the amended soil increased or was similar to that from the unamended soil, increasing after six months' incubation with F-SMS and decreasing after 12 months' incubation in all amended soils. The desorption of iprovalicarb increased with the amendment applied to all the soils, as well as after six months' incubation, and then started to decrease. This contrasting behaviour of the fungicides is probably linked to their different interaction mechanisms with the residues or with the soil components. The less hydrophobic fungicides pyrimethanil, metalaxyl and iprovalicarb might interact with specific functional groups of the residue or with the organic and inorganic moieties of the soil. Penconazole could be sorbed mainly by OM through a hydrophobic mechanism. These interaction mechanisms have been reported by Marin-Benito et al. (2012) in a FTIR study of the fungicides sorbed by SMS without soil.

4 Conclusions

The results reveal how SMS increases the sorption capacity of fungicides of different chemical classes and properties by soil amended with it at a rate of ≥ 2%. The lower DOC load and the greater degree of humification of the OC of the SMS sustained the higher sorption of all the fungicides by the soil amended with the composted SMS. The incubation of soil+SMS for 6-12 months decreased fungicide sorption, especially for the soil amended with fresh SMS at a rate of 10%. The decrease in the load of OC with incubation time was more important for explaining fungicide sorption behaviour than the changes in OC nature and structure. SMS addition enhanced the desorption of metalaxyl and iprovalicarb, but decreased that of penconazole and pyrimethanil. However, the opposite effects were observed when incubation time was increased. On the whole, the percentages of desorption were below 100% of the initial amount sorbed for all the fungicides. These results might sustain the practice of SMS addition especially in the vineyard to favour fungicide retention by soils, even after extended incubation times. This will optimise the field use of SMS reducing the leaching probability of fungicides with a different hydrophobicity to groundwater.

Acknowledgements This work was funded by the Spanish Ministry of Education and Science under project AGL2007-61674/AGR. J.M. Marín-Benito thanks Spain’s Research Council (CSIC) for his JAE-Pre-doctoral fellowship cofinanced by European and Structural and Social Funds (FEDER-FSE). We would like to thank L.F. Lorenzo, J.M. Ordax and A.

Gonzalez for their technical help, and CTICH and INTRAVAL S.L. from La Rioja, Spain, for their collaboration.

References

Ahmad R, Kookana RS, Alston AM, Skjemstad JO (2001) The nature of soil organic matter affects sorption of pesticides. 1. Relationships with carbon chemistry as determined by 13C CPMAS NMR spectroscopy. Environ Sci Technol 35:878-884

Andrades MS, Rodríguez-Cruz MS, Sánchez-Martín MJ, Sánchez-Camazano M (2004) Effect of the addition of wine distillery wastes to vineyard soils on the adsorption and mobility of fungicides. J Agric Food Chem 52:3022-3029

Arias-Estévez M, López-Periago E, Martínez-Carballo E, Simal-Gándara J, Mejuto JC, García-Río L (2008) The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agric Ecosyst Environ 123:247–260

Barriuso E, Baer U, Calvet R (1992) Disolved organic matter and adsorption-desorption of dimefuron, atrazine, and carbetamide by soils. J Environ Qual 21:359-367

Bremner JM (1996). Nitrogen total. In: Sparks DL (ed) Methods of soil analysis. Part 3-Chemical methods. Soil Science Society of America, Madison, Wisconsin, pp 1085-1121

Briceño G, Palma G, Durán N (2007). Influence of organic amendment on the biodegradation and movement of pesticides. Crit Rev Environ Sci Technol 37:233–271

Briceño G, Demanet R, Mora MD, Palma G (2008) Effect of liquid cow manure on andisol properties and atrazine adsorption. J Environ Qual 37:1519-1526

Chiou CT, Kile DE, Rutherford DW, Sheng G, Boyd, SA (2000) Sorption of selected organic compounds from water to a peat soil and its humic acid and humin fractions: Potential sources of the sorption nonlinearity. Environ Sci Technol 34:1254–1258

Chiu SW, Law SCh, Ching M, Cheung KW, Chen MJ (2000) Themes for mushroom exploitation in the 21st century: Sustainability, waste management, and conservation. J Gen Appl Microbiol 46:69–282

Clapp CE, Hayes MHB, Senesi N, Bloom PR, Jardine PM (2001) Humic substances and chemical contaminants. Soil Science of America, Madison

Cox L, Fernandes MC, Zsolnay A, Hermosín MC, Cornejo J (2004) Changes in dissolved organic carbon of soil amendments with aging: effect on pesticide adsorption behaviour. J Agric Food Chem 52:5635-5642

Cox L, Velarde P, Cabrera A, Hermosín MC, Cornejo J (2007) Dissolved organic carbon interactions with sorption and leaching of diuron in organic-amended soils. Eur J Soil Sci 58:714-721

Delgado-Moreno L, Almendros G, Peña A (2007) Raw or incubated olive-mill wastes and its biotransformed products as agricultural soil amendments effect on sorption-desorption of triazine herbicides. J Agric Food Chem 55:836-843

de Wilde T, Spanoghe P, Ryckeboer J, Jaeken P, Pringael D (2009) Sorption characteristics of pesticides on matrix substrates used in biopurification systems. Chemosphere 75:100–108

Fenoll J, Ruiz E, Flores P, Hellín P, Navarro S (2011) Reduction of the movement and persistence of pesticides in soil through common agronomic practices. Chemosphere 85:1375-1382

Fernandes MC, Cox L, Hermosín MC, Cornejo J (2006) Organic amendments affecting sorption, leaching and dissipation of fungicides is soils. Pest Manag Sci 62:1207-1215

Fernández-Bayo JD, Nogales R, Romero E (2009) Assessment of three vermicomposts as organic amendments used to enhance diuron sorption in soils with low organic carbon content. Eur J Soil Sci 60:935–944

Filipe OMS, Vidal MM, Scherer HW, Schneider RJ, Duarte AC, Esteves VI, Santos EBH (2010) Effect of long term organic amendments on adsorption–desorption of thiram onto a luvisol soil derived from loess. Chemosphere 80: 293–300

FAOSTAT (2009) Food and Agriculture Organization of the United Nations. http://faostat.fao.org. Accessed 3 August 2011

FOOTPRINT (2011) The FOOTPRINT Pesticide Properties Database (PPDB). http://sitem.herts.ac.uk/aeru/footprint/index2.htm, University of Hertfordshire

García Izquierdo C, Lobo Bedmar MC (2008) Rehabilitación de suelos degradados y contaminados mediante la aplicación de compost. In: Moreno Casco J, Moral Herrero R. (ed) Compostaje. Mundi Prensa, Madrid, pp 425-448

Ghosh RK, Singh N (2009) Effect of organic manure on sorption and degradation of azoxystrobin in soil. J Agric Food Chem 57: 632–636

Herrero-Hernández E, Andrades MS, Marín-Benito JM, Sánchez-Martín MJ, Rodríguez-Cruz MS (2011) Field-scale dissipation of tebuconazole in a vineyard soil amended with spent mushroom substrate and its potential environmental impact. Ecotox Environ Saf 74:1480–1488

López-Piñeiro A, Cabrera D, Albarrán A, Peña D (2011) Influence of two-phase olive mill waste application to soil on terbuthylazine behaviour and persistence under controlled and field conditions. J Soils Sediments 11:771–782

Luo JM, Liu MC, Zha J, Wang Z (2009) Impacts of particulate organic carbon and dissolved organic carbon on removal of polycyclic aromatic hydrocarbons, organochlorine pesticides, and nonylphenols in a wetland. J Soils Sediments 9:180–187

MAPA (Ministerio de Agricultura, Pesca y Alimentación) (1986) Métodos oficiales de análisis. Dirección General de Política Alimentaría, Madrid

Marin-Benito JM (2011) Dinámica de fungicidas en suelos de viñedo enmendados con substrato postcultivo de hongos. Dissertation. University of Salamanca

Marín-Benito JM, Sánchez-Martín MJ, Andrades MS, Pérez-Clavijo M, Rodríguez-Cruz MS (2009a) Effect of spent mushroom substrate amendment of vineyard soils on the behaviour of fungicides: 1. Adsorption-desorption of penconazole and metalaxyl by soils and sub-soils. J Agric Food Chem 57:9634–9642

Marín-Benito JM, Rodríguez-Cruz MS, Andrades MS, Sánchez-Martín MJ (2009b) Effect of spent mushroom substrate amendment of vineyard soils on the behavior of fungicides: 2. Mobility of penconazole and metalaxyl in undisturbed soil cores. J Agric Food Chem 57:9643-9650

Marín-Benito JM, Rodríguez-Cruz MS, Andrades MS, Sánchez-Martín MJ (2012) Assessment of spent mushroom substrate as sorbent of fungicides: influence of sorbent and sorbate properties. J Environ Qual (in press) doi:10.2135/jeq2011.0437

Miguéns T, Leirós C, Gil-Sotres F, Trasar-Cepeda C (2007) Biochemical properties of vineyard soils in Galicia, Spain. Sci Total Environ 378:218–222

Müller K, Magesan GN, Bolan NS (2007) A critical review of the influence of effluent irrigation on the fate of pesticides in soil. Agr Ecosyst Environ 120: 93-116

Nelson DW, Sommers LE (1996) Total carbon, organic carbon and organic matter. In: Sparks DL (ed), Methods of soil analysis. Part 3-Chemical methods. Soil Science Society of America Inc, Madison, Wisconsin, pp 961-1010

Reichenberger S, Bach M, Skitschak A, Frede HG (2007) Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness: a review. Sci Total Environ 384:1–35

Rodríguez-Cruz MS, Ordax JM, Arienzo M, Sánchez-Martín MJ (2011) Enhanced retention of linuron, alachlor and metalaxyl in sandy soil columns intercalated with wood barriers. Chemosphere 82:1415–1421

Sánchez L, Romero E, Sánchez-Rasero F, Dios F, Peña A (2003) Enhanced soil sorption of methidathion using sewage sludge and surfactants. Pest Manag Sci 59:857-864

Sánchez-Camazano M, Iglesias-Jiménez E, Sánchez-Martin MJ (1997) City refuse compost and sodium dodecyl sulphate as modifiers of diazinon leaching in soil. Chemosphere 35:3003-3012

Sheng G, Johnson CT, Teppen BJ, Boyd SA (2001) Potential contribution of smectite clays and organic matter to pesticide retention in soils. J Agric Food Chem 49:2899–2907

Soil Survey Staff (2006) Keys to soil taxonomy. United States Department of Agriculture (USDA), Natural Resources Conservation Service, Washington DC

Spokas KA, Koskinen WC, Baker JM, Reicosky DC (2009) Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77:574–581

Stevenson FJ (1982) Humus chemistry. Genesis-composition-reactions. John Wiley and Sons, New York

Tomlin CDS (2000) The pesticide manual. British Crop Protection Council, Cambridge

Wauchope RD, Yeh S, Linders JBHJ, Kloskowski R, Tanaka K, Rubin B, Katayama A, Kördel W, Gerstl Z, Lane M, Unsworth JB (2002) Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Manag Sci 58:419-445

Wang H, Lin K, Hou Z, Richardson B, Gan J (2010) Sorption of the herbicide terbuthylazine in two New Zealand forest soils amended with biosolids and biochars. J Soils Sediments 10:283–289

Wuest PJ, Levanon D, Hadar Y (1995) Environmental, agricultural and industrial uses for spent mushroom substrate from mushroom farms. J G Press, Emmaus

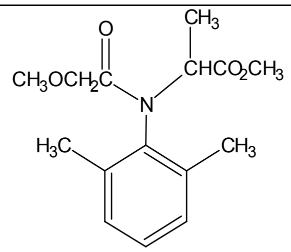
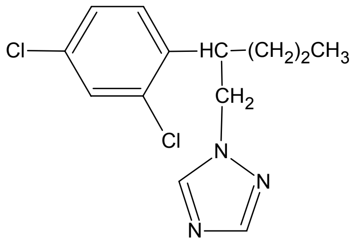
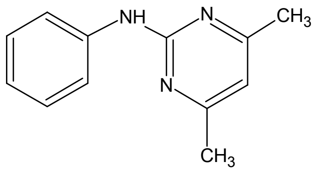
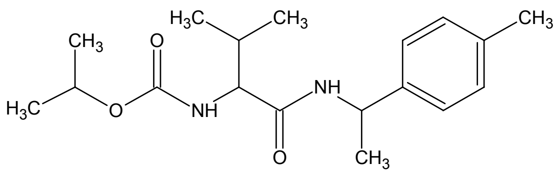
Zhang W, Xu M, Wang X, Huang Q, Nie J, Li Z, Li S, Hwang SW, Lee KB (2012) Effects of organic amendments on soil carbon sequestration in paddy fields of subtropical China. J Soils Sediments. doi:10.1007/s11368-011-0467-8

Figure legends

Fig. 1 Sorption-desorption isotherms of fungicides in unamended soil (Al), soil amended with composted spent mushroom substrate at rates of 2% (*Al+C-SMS2*) and 10% (*Al+C-SMS10*), and soil amended with fresh spent mushroom substrate at rates of 2% (*Al+F-SMS2*) and 10% (*Al+F-SMS10*). Error bars represent standard deviation of the mean value

Fig. 2 Desorbed amounts of fungicide from unamended soil (Al), soil amended with composted spent mushroom substrate at rates of 2% (*Al+C-SMS2*) and 10% (*Al+C-SMS10*), and soil amended with fresh spent mushroom substrate at rates of 2% (*Al+F-SMS2*) and 10% (*Al+F-SMS10*) initially treated with 25 mg L^{-1} of penconazole, pyrimethanil and metalaxyl solution or 5 mg L^{-1} of iprovalicarb solution after four successive desorption stages and at 0, 6 and 12 months of soil+SMS incubation. Error bars represent standard deviation of the mean value

Table 1. Chemical structure and characteristics of fungicides

Common name Chemical name	Chemical structure	WS (mg L^{-1})[a]	log Kow[a]	Koc (mL g^{-1})[a]	Half life ($days^{-1}$)[a]
Metalaxyl Methyl *N*-methoxyacetyl-N-2,6-xylyl-DL-alaninate		8400	1.75	28-284	42-46
Penconazole 1-(2,4-dichloro-β-propylphenetyl-1*H*-1,2,4-triazole		73	3.72	786-4120	22-207
Pyrimethanil *N*-(4,6-dimethylpyrimidin-2-yl) aniline		121	2.84	75-500	23-71.8
Iprovalicarb Isopropyl 2-methyl-1-[(1-p-tolylethyl) carbamoyl]-(S)-propylcarbamate		11	3.2	106	4.7-30

WS Solubility in water at 20ºC, Kow Octanol/water partition coefficient at pH 7 and 20ºC, Koc Sorption coefficient normalized to organic carbon content. [a]From FOOTPRINT (2011) and Tomlin (2000)

Table 2. Characteristics of spent mushroom substrates given on a dry weigh basis

Characteristics	C-SMS	F-SMS
pH (1:2 ratio)	7.5	4.5
Ash %	48.3	32.5
Moisture %	32.5	55.3
OM (100-ash%)	51.7	67.5
OC %	26.7	31.2
N total (%)	2.24	1.75
C/N	12.5	17.9
DOC %	1.22	10.8
HA (%)	3.21	4.52
FA (%)	1.32	9.21
HA/FA	2.43	0.49
Cd (mg/kg)	0.32	0.14
Cr (mg/kg)	89.4	3.72
Cu (mg/kg)	38.1	5.76
Ni (mg/kg)	28.4	2.42
Pb (mg/kg)	29.6	2.78
Zn (mg/kg)	180	292
Hg (mg/kg)	0.03	<0.01

OM organic matter, OC organic carbon, DOC water soluble organic carbon, HA alkali soluble organic carbon, FA acid and alkali soluble organic carbon, C-SMS composted spent mushroom substrate, F-SMS fresh spent mushroom substrate

Table 3. Characteristics of unamended and amended soils after 0, 6 and 12 months of incubation

Time of treatment/Soil	pH	OC (%)	DOC (mg g^{-1})	HA (mg g^{-1})	FA (mg g^{-1})	HA/FA
0 months						
Al	7.87	0.59	0.046	0.432	0.563	0.767
Al+C-SMS2	7.73	1.28	0.193	0.670	0.754	0.888
Al+C-SMS10	7.44	3.81	0.817	2.079	1.872	1.110
Al+F-SMS2	7.26	1.43	1.120	0.764	2.170	0.352
Al+F-SMS10	6.04	3.96	10.47	2.662	9.562	0.278
6 months						
Al	7.89	0.53	0.045	-	-	-
Al+C-SMS2	7.70	1.10	0.204	-	-	-
Al+C-SMS10	7.41	3.10	0.425	-	-	-
Al+F-SMS2	7.64	0.90	0.119	-	-	-
Al+F-SMS10	7.70	1.95	1.007	-	-	-
12 months						
Al	7.84	0.58	0.036	0.357	0.621	0.575
Al+C-SMS2	7.65	1.18	0.079	0.717	0.758	0.946
Al+C-SMS10	7.47	3.12	0.364	2.439	1.631	1.495
Al+F-SMS2	7.88	0.95	0.158	0.526	0.977	0.538
Al+F-SMS10	7.90	1.78	0.706	2.069	2.841	0.728

Al unamended soil, Al+C-SMS2 soil amended with composted spent mushroom substrate at rate of 2%, Al+C-SMS10 soil amended with composted spent mushroom substrate at rate of 10%, Al+F-SMS2 soil amended with fresh spent mushroom substrate at rate of 2%, Al+F-SMS10 soil amended with fresh spent mushroom substrate at rate of 10%

Table 4. Ranges of Freundlich constants for the sorption of fungicides by unamended Al soil and Al soil amended with composted (Al+C-SMS10 and Al+C-SMS2) and fresh (Al+F-SMS10 and Al+F-SMS2) spent mushroom substrate after 0, 6 and 12 months of incubation.

Fungicide	0 months		6 months		12 months	
	Kf (SD)	nf (SD)	Kf (SD)	nf (SD)	Kf (SD)	nf (SD)
Metalaxyl	0.23-1.56	0.81-1.06	0.27-1.52	0.86-0.94	0.23-1.21	0.87-0.95
	(0.01-0.07)	(0.01-0.04)	(0.01-0.02)	(0.00-0.03)	(0.00-0.02)	(0.00-0.04)
Penconazole	5.17-31.8	0.83-0.96	4.88-26.6	0.83-0.90	4.67-23.5	0.82-0.92
	(0.00-0.39)	(0.00-0.02)	(0.02-0.64)	(0.00-0.02)	(0.00-0.18)	(0.00-0.01)
Pyrimethanil	1.70-12.6	0.74-0.92	1.71-10.4	0.85-0.94	1.81-10.2	0.80-0.89
	(0.10-0.58)	(0.04-0.09)	(0.03-0.33)	(0.00-0.07)	(0.00-0.22)	(0.00-0.06)
Iprovalicarb	0.44-3.41	0.72-1.05	0.48-3.24	0.86-1.00	0.19-2.45	0.83-1.07
	(0.01-0.15)	(0.01-0.19)	(0.00-0.09)	(0.01-0.18)	(0.02-0.03)	(0.01-0.08)

Al+C-SMS2 soil amended with composted spent mushroom substrate at rate of 2%, Al+C-SMS10 soil amended with composted spent mushroom substrate at rate of 10%, Al+F-SMS2 soil amended with fresh spent mushroom substrate at rate of 2%, Al+F-SMS10 soil amended with fresh spent mushroom substrate at rate of 10%, Ranges of standard deviations (SD) of Kf and nf Freundlich sorption constants are indicated in parenthesis.

Table 5. Distribution coefficients (Kd) for the sorption of fungicides by unamended soil and soil amended with composted and fresh spent mushroom substrate after 0, 6 and 12 months of incubation and organic carbon normalised coefficients (Koc)

Fungicide	0 months		6 months		12 months	
Soil	Kd±SD	Koc	Kd±SD	Koc	Kd±SD	Koc
Metalaxyl						
Al	0.20±0.01a	37.0	0.23±0.00 [a]	43.4	0.22±0.00	37.9
Al+C-SMS2	0.49±0.00c	38.3	0.42±0.01 [a]	38.2	0.43±0.01 [a]	36.4
Al+C-SMS10	1.30±0.01e	34.1	1.22±0.00 [a]	39.4	1.02±0.00 [a]	32.7
Al+F-SMS2	0.25±0.00b	17.5	0.26±0.01	28.9	0.26±0.01	27.4
Al+F-SMS10	0.70±0.00d	17.7	0.48±0.01 [a]	24.6	0.48±0.01 [a]	27.0
Mean		28.9		34.9		32.3
CV (%)		36.2		22.4		15.6
Penconazole						
Al	3.95±0.10a	731	3.73±0.07	703	3.48±0.04 [a]	600
Al+C-SMS2	9.77±0.07b	763	6.88±0.06 [a]	625	7.80±0.13 [a]	661
Al+C-SMS10	26.5±0.45e	695	21.6±0.71 [a]	696	18.7±0.04 [a]	599
Al+F-SMS2	6.83±0.21c	477	5.20±0.27 [a]	577	5.10±0.09 [a]	536
Al+F-SMS10	15.2±0.38d	383	9.80±0.08 [a]	502	9.47±0.08 [a]	532
Mean		610		621		585
CV (%)		27.7		13.6		9.1
Pyrimethanil						
Al	1.12±0.10a	207	1.39±0.07	262	1.32±0.01	227
Al+C-SMS2	2.92±0.26b	228	2.89±0.16	262	2.99±0.09	253
Al+C-SMS10	9.88±0.39d	259	8.84±0.25 [a]	285	8.02±0.17 [a]	257
Al+F-SMS2	1.93±0.10ab	135	1.83±0.03	203	1.73±0.04	182
Al+F-SMS10	6.89±0.91c	174	3.78±0.08 [a]	193	3.07±0.04 [a]	172
Mean		200		241		218
CV (%)		24.0		16.7		18.1
Iprovalicarb						
Al	0.69±0.01ab	128	0.51±0.01	96.2	0.70±0.01	120
Al+C-SMS2	0.79±0.01b	61.7	0.44±0.00 [a]	40.0	1.26±0.04 [a]	106
Al+C-SMS10	3.12±0.07d	81.9	3.05±0.01	98.4	2.34±0.01 [a]	75.0
Al+F-SMS2	0.43±0.06a	30.1	0.64±0.01 [a]	71.1	0.17±0.06 [a]	17.9
Al+F-SMS10	2.23±0.27c	56.3	0.85±0.01 [a]	43.6	1.05±0.04 [a]	59.0
Mean		71.6		69.9		75.9
CV (%)		51.0		39.8		53.6

Al unamended soil, Al+C-SMS2 soil amended with composted spent mushroom substrate at rate of 2%, Al+C-SMS10 soil amended with composted spent mushroom substrate at rate of 10%, Al+F-SMS2 soil amended with fresh spent mushroom substrate at rate of 2%, Al+F-SMS10 soil amended with fresh spent mushroom substrate at rate of 10%, Kd distribution coefficients are indicated as mean values ± standard deviation

a,b,c,d,e, Kd values at 0 months followed with the same letter are not significantly different ($p<0.05$), [a] Kd values in the same raw at 6 months and 12 months are significantly different of Kd values at 0 months ($p<0.05$)

Table 6. Multiple regression equations between distribution coefficients of fungicides and organic carbon and dissolved organic carbon.

Fungicide	Regression equation	Significance level		R^2
		OC	DOC	
Metalaxyl	Kd = -0.042+0.365 OC – 0.068 DOC	0.020	0.066	96.0
Penconazole	Kd = -0.391+7.322 OC – 1.296 DOC	0.007	0.027	98.6
Pyrimethanil	Kd = -0.897+2.877 OC – 0.353 DOC	0.011	0.082	98.1
Iprovalicarb	Kd = -0.204+0.866 OC – 0.099 DOC	0.049	0.293	91.0

Kd distribution coefficients of fungicides, OC organic carbon, DOC dissolved organic carbon

Table 7. Ranges of Freundlich constants for the desorption of fungicides from unamended Al soil and Al soil amended with composted (Al+C-SMS2 and Al+C-SMS10) and fresh (Al+F-SMS2 and Al+F-SMS10) spent mushroom substrate after 0, 6 and 12 months of incubation.

Fungicide	0 months		6 months		12 months	
	Kfd (SD)	nfd (SD)	Kfd (SD)	nfd (SD)	Kfd (SD)	nfd (SD)
Metalaxyl	1.34-3.70	0.36-0.60	0.71-3.18	0.43-0.65	1.26-3.97	0.21-0.61
	(0.01-0.24)	(0.01-0.04)	(0.03-0.39)	(0.01-0.06)	(0.03-0.52)	(0.00-0.06)
Penconazole	14.4-44.7	0.11-0.36	13.2-42.7	0.13-0.39	13.8-40.8	0.14-0.35
	(0.03-2.63)	(0.01-0.05)	(0.47-1.68)	(0.01-0.02)	(0.19-0.53)	(0.01-0.02)
Pyrimethanil	2.31-31.7	0.19-0.67	5.48-27.4	0.26-0.47	3.56-22.3	0.36-0.57
	(0.15-1.52)	(0.00-0.09)	(1.09-2.98)	(0.03-0.10)	(0.18-0.86)	(0.01-0.03)
Iprovalicarb	1.10-3.59	0.09-0.66	0.51-3.56	0.12-0.88	0.39-3.34	0.08-1.09
	(0.03-0.52)	(0.00-0.08)	(0.00-0.43)	(0.00-0.08)	(0.03-0.37)	(0.00-0.03)

Al+C-SMS2 soil amended with composted spent mushroom substrate at rate of 2%, Al+C-SMS10 soil amended with composted spent mushroom substrate at rate of 10%, Al+F-SMS2 soil amended with fresh spent mushroom substrate at rate of 2%, Al+F-SMS10 soil amended with fresh spent mushroom substrate at rate of 10%, Ranges of standard deviations (SD) of Kfd and nfd Freundlich desorption constants are indicated in parenthesis

Table 8. Hysteresis coefficients for the desorption of fungicides by unamended and amended soil after 0, 6 and 12 months of incubation.

Fungicide Soil	0 months H±SD	6 months H±SD	12 months H±SD
Metalaxyl			
Al	2.45±0.22	1.56±0.07	4.59±1.27
Al+C-SMS2	2.04±0.19	2.07±0.36	2.47±0.09
Al+C-SMS10	1.49±0.02	1.47±0.02	1.87±0.19
Al+F-SMS2	2.93±0.30	1.78±0.10	3.05±0.04
Al+F-SMS10	1.44±0.07	1.36±0.09	1.42±0.19
Penconazole			
Al	2.28±0.26	2.15±0.08	2.35±0.07
Al+C-SMS2	4.99±1.47	3.05±0.08	3.33±0.07
Al+C-SMS10	8.18±0.62	6.75±0.48	6.31±0.46
Al+F-SMS2	2.66±0.16	2.42±0.20	2.51±0.04
Al+F-SMS10	3.39±0.58	2.90±0.30	2.82±0.15
Pyrimethanil			
Al	1.10±0.03	1.94±0.41	1.46±0.04
Al+C-SMS2	1.62±0.19	2.25±0.53	1.63±0.19
Al+C-SMS10	4.40±0.02	3.49±0.67	2.37±0.06
Al+F-SMS2	1.51±0.15	1.90±0.34	1.79±0.07
Al+F-SMS10	1.58±0.09	2.32±0.21	1.57±0.07
Iprovalicarb			
Al	10.1±1.08	7.30±1.69	13.2±0.67
Al+C-SMS2	2.24±0.02	1.38±0.38	7.02±0.22
Al+C-SMS10	1.32±0.06	1.41±0.16	0.86±0.03
Al+F-SMS2	4.39±1.05	1.12±0.25	1.95±0.46
Al+F-SMS10	1.71±0.36	2.14±0.07	3.77±0.47

Al unamended soil, Al+C-SMS2 soil amended with composted spent mushroom substrate at rate of 2%, Al+C-SMS10 soil amended with composted spent mushroom substrate at rate of 10%, Al+F-SMS2 soil amended with fresh spent mushroom substrate at rate of 2%, Al+F-SMS10 soil amended with fresh spent mushroom substrate at rate of 10%, H hysteresis coefficients are indicated as mean values ± standard deviation.

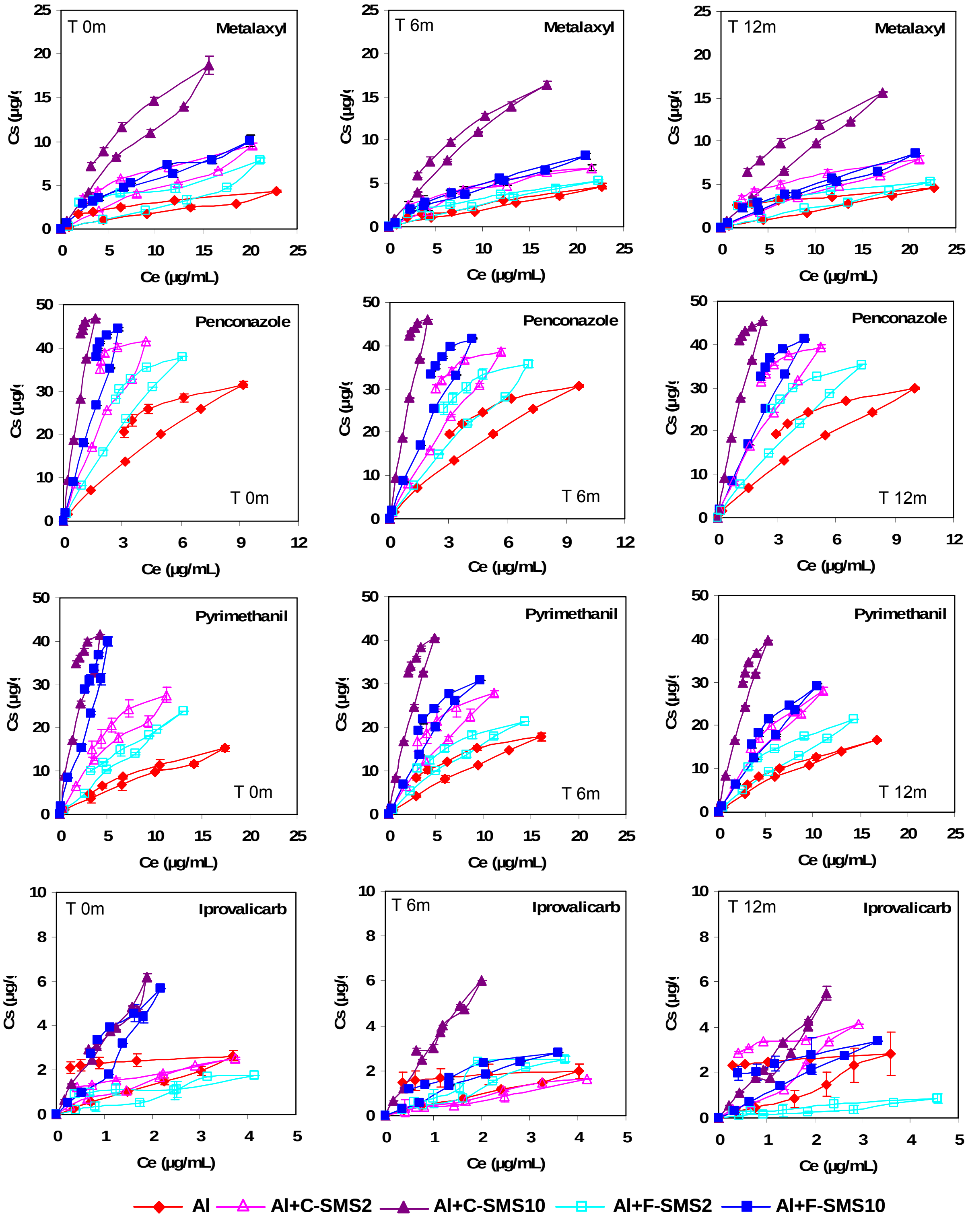

T 0m
Metalaxyl
T 6m
Metalaxyl
T 12m
Metalaxyl
Penconazole
T 0m
Penconazole
T 6m
Penconazole
T 12m
Pyrimethanil
T 0m
Pyrimethanil
T 6m
Pyrimethanil
T 12m
T 0m
Iprovalicarb
T 6m
Iprovalicarb
T 12m
Iprovalicarb
Ce (µg/mL)
Al
Al+C-SMS2
Al+C-SMS10
Al+F-SMS2
Al+F-SMS10

Fig 1

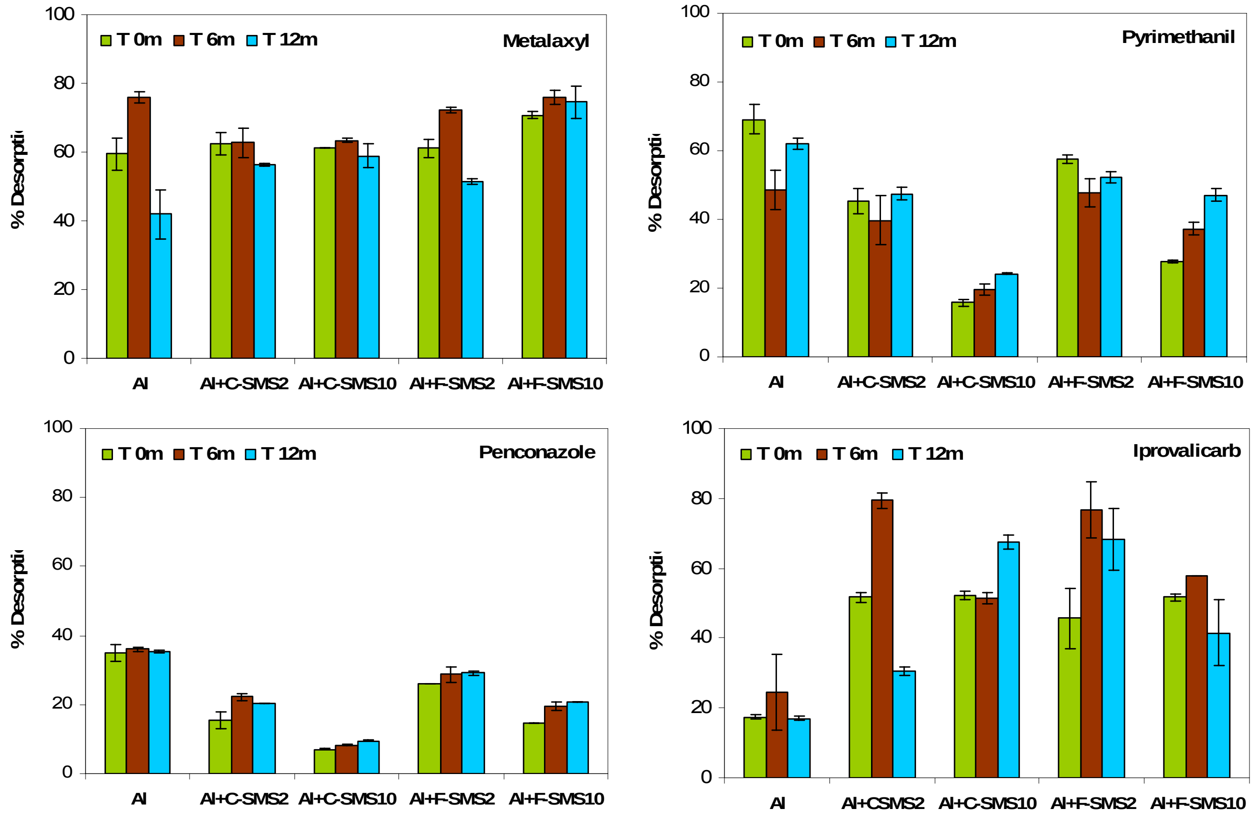

T 0m
T 6m
T 12m
Metalaxyl
Pyrimethanil
Penconazole
Iprovalicarb
% Desorpti
100
80
60
40
20
0
Al
Al+C-SMS2
Al+C-SMS10
Al+F-SMS2
Al+F-SMS10
Al+CSMS2

Fig 2