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Article

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Comparative sorption and leaching study of the herbicides fluometuron and MCPA in a soil amended with biochars and other sorbents

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Abstract

Biochar, the solid residual remaining after the thermo-chemical transformation of biomass for carbon sequestration has been proposed to be used as soil amendment, because of its agronomic benefits. The effect of amending soil with 6 biochars made from different feedstocks on sorption and leaching of fluometuron and 4-chloro-2-methyl phenoxyacetic acid (MCPA) was compared to the effect of other sorbents: an activated carbon, a Ca-rich Arizona montmorillonite modified with hexadecyltrimethylammonium organic cation (SA-HDTMA), and an agricultural organic residue from olive oil production (OOW). Soil was amended at 2% (w/w) and studies were performed following a batch equilibration procedure. Sorption of both herbicides increased in all amended soils, but decreased in soil amended with a biochar produced from macadamia nut shells made with fast pyrolysis. Lower leaching of the herbicides was observed in the soils amended with the biochars with higher surface areas BC5, BC6 and the organoclay (OCl). Despite the increase in herbicide sorption in soils amended with two hardwood biochars (BC1, and BC3), and OOW, leaching of fluometuron and MCPA was enhanced with the addition of these amendments as compared to the unamended soil. The increased leaching is due to some amendments´ soluble organic compounds, which compete or associate with herbicide molecules enhancing their soil mobility. Thus, our results indicate that not all biochar amendments will increase sorption and decrease leaching of fluometuron and MCPA. Furthermore, the amount and composition of the organic carbon (OC) content of the amendment, specially the soluble part (DOC) can play an important role on sorption and leaching of these herbicides.

Keywords: Amendment, biochar, dissolved organic carbon, fluometuron, herbicides, leaching, MCPA, olive oil mill waste, organoclay, pesticides, soil, sorption.

Introduction

Large amounts of pesticides are used on agricultural soils worldwide because they increase crop yields, ensuring an abundant and affordable food supply. However, the risk of surface and groundwater contamination is of concern because of the potential negative consequences for human health and the environment *(1)*. Therefore, it is essential to know and understand the fate of pesticides in soil prior to implementing pest management strategies.

Fluometuron (*N,N*-dimethyl-*N*′-[3-(trifluoromethyl)phenyl]urea) is a phenylurea herbicide used for the pre-emergence and early post-emergence control of weeds in cotton crops. Sorption of fluometuron is influenced by the organic matter (OM) content of the soil *(2)* and high mobility and leaching of the herbicide has been reported for soils with low OM content *(2,3)*. According to Baskaran and Kennedy *(4)* this herbicide can leach through permeable and sandy soils and may result in groundwater contamination.

MCPA (4-chloro-2-methylphenoxyacetic acid) is a weak acid herbicide used for the control of a broad spectrum of weeds in pre-emergence in a variety of crops. At natural agricultural soil pH levels, MCPA is in the anionic form, and as other anionic herbicides is weakly sorbed to soil. Thus, MCPA is highly mobile, with runoff and leaching risks for surface and groundwater *(5)*. The addition of a variety of organic amendments to agricultural soils is a common practice to increase soil OM content. Biochar, the solid residue remaining after the thermo-chemical transformation of biomass, has been recently proposed as soil amendment *(6)*, because of its high stability against decay in soil environments *(7)*, and its apparent ability to influence the availability of nutrients as compared to other soil organic amendments. Biochar is considered more biologically inert as compared to other forms of organic C in soil due to its highly

condensed aromatic structure *(8)*. Therefore, biochar applications can simultaneously achieve both C sequestration and soil fertility improvements. The effects of the use of biochar as soil amendment on soil properties has been extensively studied and reported *(9,10)*.

Other organic wastes have also been suggested as soil amendments, such as sewage sludge, spent mushroom substrates, and wastes from urban, olive mills, and wineries. These additions have been shown to increase sorption of pesticides *(11-14)*. These amendments have also been shown to influence other pesticide soil processes, such as leaching and degradation *(12,15)*. In contrast, there are few studies about the impacts of biochar on pesticides fate in soils (*16,17)*. Addition of biochar has been shown to increase sorption and to decrease the dissipation of pesticides in soils *(18-20)*. For these reasons, biochar could be postulated as an amendment to potentially reduce the contamination risks of surface and ground waters if mixed with soils as inmobilization zone, which is the hypothesis of this work. The aim of this work was to assess the potential of several biochars made from different feedstocks under different pyrolysis condition to increase the sorption and reduce the vertical mobility of the herbicides fluometuron and MCPA in a sandy soil. These herbicides were selected for the study, due to their wide use in common crops, such as cotton, cereals, olive and vines, and to the high mobility and leaching risk reported for both herbicides. The biochars were also compared with other proposed soil amendments, such as activated carbon, olive mill waste (OOW), and an organically modified clay. OOW is a solid waste produced by the two-phase centrifugation process for the olive oil extraction. This waste is rich in OM and its use as soil amendment is an efficient way for its disposal, and has shown to increase the sorption of herbicides *(13,21-24)*. Organoclays (OCls) are natural mineral clays, in which the inorganic exchange cation has been replaced with organic cations. The use of OCls has

been proposed to reduce the risk of transport of organic contaminants from soil *(25),* and recently as soil amendments *(26)* to improve the fate of herbicides in soils.

Materials and methods

Herbicides

Fluometuron (Figure 1) is a substituted urea, which has a water solubility of 105 mg L^{-1} at 20 ºC and pH = 7 *(27)*. Pure analytical fluometuron (purity = 99.5%) purchased from Sigma-Aldrich (Spain) was used to prepare the external standards for fluometuron analysis and the initial solutions used in the batch sorption experiments. Commercial fluometuron (Dinagam Linz, 50% suspension concentrate) from Bayer (Spain) was used in the column leaching experiments.

MCPA (Figure 1) is a weak acid with a water solubility of 293.9 mg L^{-1} at 25 ºC and pH = 7 *(27)*. Analytical grade MCPA (purity = 98.9%) from Riedel-de Haën (Germany) was used to prepare the initial herbicide solutions used in the adsorption and leaching experiments, and the external standards for herbicide analysis.

Amendments

Six different biochars, ranging in characteristics and origins, were used as sorbents (Table 1). Two biochars were activated by thermal (BC4) and chemical (BC6) processes to study if biochar activation increases their sorptive properties. Thermal activation was achieved by heating the biochar to 200 ºC in the presence of atmospheric oxygen for 24 h. Chemical activation for BC6 was obtained by a 24 h soaking in 3% hydrogen peroxide (H_2O_2) which was following by air drying to remove easily oxidized organics. Biochars were characterized by total elemental

composition (Ultimate Analysis, ASTM D3176-09). Specific surface area of biochar was measured by nitrogen surface sorption, using a Carlo Erba Sorptomatic 1900 and the Brunauer, Emmett, and Teller (BET) method on previously degassed 0.2 g of sample at 80 ºC during 24 h. The untreated biochars had the lowest surface areas (3.3 to 46 $m^2 g^{-1}$), whereas the activated charcoal possessed a surface area of 979 $m^2 g^{-1}$.

The pH was determined by a 1:5 biochar to deionized water slurry. The pH values for the biochars ranged from 5.5 to 8.0. Carbon contents were determined with ASTM method D5373-08 and correspondingly ranged from 44 to 95% and nitrogen content from 0.3 to 1.3%.

Dissolved organic carbon (DOC) from amendments was characterized and extracted by treatment of 1 g of the sorbent with 20 mL of 0.01M $CaCl_2$. Suspensions were shaken overnight and centrifuged at 10000 rpm during 10 min and filtered through a 0.45 μm pore nylon filter. DOC of the extracts was measured with a Shimadzu TOC-V sch.

The organoclay (OCl) was synthesized by modifiying Ca-rich Arizona montmorillonite (Clay Minerals Society, Purdue University) with the organic cation hexadecyltrimethylammonium (HDTMA). Modification was carried out through an ion exchange reaction by treating 10 g of the montmorillonite with 100 mL of an ethanol/water (50:50) solution containing an amount of the organic cation equal to the CEC of the clay (CEC = 120 cmol kg^{-1}). The suspension was shaken for 24 h, centrifuged, washed with distilled water until Cl-free, and then lyophilized. Organic cation was supplied by Sigma-Aldrich as high-purity chloride salt (purity > 98%).

The OOW was kindly supplied by the experimental olive oil mill IFAPA Venta del Llano, located in Mengíbar (Jaén, Spain). To reduce its high moisture content the OOW was air dried prior to use. Properties of the waste were: pH 5.8, OM 92% and C:N ratio 39.

Soil

The soil used was a sandy loam soil with 79% sand, 8% silt, and 13% clay; it has an OC content of 0.25%, 0.43% OM, 0.03% N org and C/N ratio equal to 8. This soil was located in the experimental farm of IRNAS (Coria del Río, Sevilla, Spain) and devoted to olive groves. Soil was amended at a rate of 2% (w/w) with the sorbent for the sorption-desorption experiments. Soil and amendments were thoroughly mixed and sieved with a 2 mm mesh sieve. OC content of the amended soils increased in a range of 0.69-2.14%, depending on the amendment and according to the 2% w:w amending rate.

Sorption-desorption experiments

Duplicate samples (2.5 g) of unamended and 2% (w/w) amended soils were treated with 5 mL of fluometuron and MCPA solutions (initial concentrations, Ci, ranged from 1 to 20 mg L^{-1} in 0.01 M $CaCl_2$). Previously, it was determined that equilibrium was reached in < 24 h and that no measurable degradation occurred during this period. Equilibrium concentrations (Ce) in the supernatants after 24 h of equilibration time were determined by HPLC with a Waters 600E chromatograph coupled to a Waters 996 diode-array detector, under the following conditions: Nova-Pack column, 150 mm length x 3.9 mm i.d.; column packing, C18; flow rate, 1 mL min^{-1}; 25 µL injection; eluent system for fluometuron 60:40 (v:v) water/acetonitrile mixture and UV detection at 243 nm, and eluent system for MCPA 60:40 (v:v) methanol/diluted H_3PO_4 (pH = 2) mixture and UV detection at 230 nm. Differences between Ci and Ce were assumed to be the amounts sorbed (Cs). Sorption isotherms were fitted to the Freundlich equation, $Cs = Kf \cdot Ce^{1/nf}$, and sorption coefficients Kf and 1/nf calculated. Kd-15 was calculated as Cs/Ce at 15 mg L^{-1} as Ce. Herbicide desorption was made with successive washings (three times) with 0.01 M $CaCl_2$ of the soil that was initially equilibrated with 20 mg L^{-1} herbicide concentration for 24 h. And hysteresis coefficient was determined as $H = 1/nf_{des} / 1/nf_{ads}$.

156

157 Leaching experiments

158 Duplicate columns (3.1 cm i.d.) were hand-packed with 150 g unamended soils to a height of 20
159 cm soil in each column. To study the amendment effect on leaching 10 g of soil amended with
160 2% of sorbent was placed at the top of the soil. Glass wool was placed at the bottom of the
161 column to avoid soil losses, and sea sand was added at the top of the soil or amended soil. After
162 saturation of the soils with 0.01 M $CaCl_2$, solutions of fluometuron or MCPA in methanol were
163 added to the soil in the column at a rate of 2 kg ha^{-1} (0.15 mg a.i.). After 24 h, enough time for
164 the methanol to evaporate, 10 mL of 0.01 M $CaCl_2$ was added daily and the leachates were
165 collected during 30 days. The leachates were analyzed by HPLC, as previously described. At the
166 end of the leaching study, soil was extracted from the columns aided by N_2 gas and sectioned
167 into 5 cm increments corresponding to different depths; fluometuron was extracted with
168 methanol, and MCPA with a mixture of 60:40 (v:v) methanol/diluted H_3PO_4 (pH = 2). Extracts
169 were centrifuged, filtered and analyzed by HPLC as previously described. Percentage of the
170 herbicides leached was plotted against the volume added to obtain the breakthrough and
171 cumulative breakthrough curves.

172

173 **Results and discussion**

174 **Sorption-desorption experiments**

175 **Fluometuron**

176 Sorption isotherms are shown in Figure 2 and Freundlich sorption and desorption coefficients in
177 Table 2. From the Figure 2a, and b it is observed that soil+amendment mixtures resulted in three
178 levels of isotherms: of high sorption (S+AC, S+OCl, S+BC5 and S+BC6), medium sorption
179 (S+BC1, S+BC3 and S+BC4); and low sorption (S+OOW and S+BC2). Unamended soil also

had low sorption. With the exception of isotherms corresponding to soil with AC and OCl, all isotherms were of L type. Sorption data fit the Freundlich equation (R^2 = 0.917-0.997). Fluometuron was completely sorbed in the soil amended with the activated carbon and data could not be fitted to Freundlich equation. The slopes of the isotherms (1/nf) are lower than unity, which means that sorption is highly dependent on initial solution concentration, with proportionally higher sorption at lower concentration as compared to higher concentrations *(28).*

Fluometuron Kf value in the unamended soil was 0.44 (Table 2), slightly lower than values reported in the literature 0.56-1.29 for soils with 0.65-1.27% OC content *(4)*, and 1.04-2.18 for conventional tillage surface soil with 0.4-2% OC content and 0-25 cm depth *(29)*, but in the order of data reported by Locke et al. *(30)*, Kf values of 0.42-1.56 on conventional tillage surface with 0.46-1.13% OC. Due to the fact that 1/nf values were not equal, Kd-15 (sorption coefficients at Ce = 15 mg L^{-1}) values were used to compare sorption of fluometuron (Table 2), and followed the trend: S+OCl > S+BC5 > S+BC6 > S+BC4 > S+BC3 ≥ S+BC1 > S+OOW > S+BC2 > S.

Sorption of fluometuron is related to the DOC content and the surface area of biochar. High sorption of fluometuron was observed in the soil amended with BC5 and BC6, whose surface areas were 46 and 16.2 m^2 g^{-1}, respectively. However, lower sorption of fluometuron was observed in the soil amended with BC2, with the higher content on DOC (352 mg L^{-1}) and lowest surface area (3.29 m^2 g^{-1}) (Table 1). The low sorption of fluometuron can be attributed to the competition between the DOC and herbicide molecules for sorption sites and by interactions in solution between fluometuron and the DOC, as was reported for diuron, another substituted urea herbicide by Cox et al. *(31)*. DOC on soil also modifies the hydrophobic and/or hydrophilic character of the soil, reducing its affinity for pesticide sorption *(32)*. Yu et al. *(20)* related the

sorption of the fungicide pyrimethanil in a sandy loam soil amended with biochar to the specific surface area (SSA) of the amendment. These authors reported higher sorption of the fungicide in the soil amended with the biochar with higher SSA. Also BC5 and BC6 are produced from wood pellets in a slow pyrolysis limited-aerobic process, which were separated by sieving (> and < 2 mm), yielding fractions of the same biochar with different particle sizes. BC5 is the lower particle size (< 2 mm) and BC6 is the biochar of higher particle size (> 2 mm), which was also activated with 3% hydrogen peroxide (H_20_2). Despite the biochar activation higher sorption of fluometuron was observed in the soil amended with the biochar with lower particle size, and hence higher SSA (BC5) (Table 1).

Sorption of fluometuron on the soil amended with the modified clay was even higher than in the soils amended with biochars, a 1.8-to-25.2-fold increase was observed for the Kd-15 values (Table 2). Fluometuron Kd-15 calculated for the soil amended with the organoclay was 5.6, a 31-fold increase as compared to the unamended soil. A high affinity of the herbicide fluometuron for the organoclay SA-HDTMA has been reported *(26)*, and attributed to hydrophobic interactions between fluometuron and the alkyl chains of HDTMA cations.

When OOW was studied as a fluometuron sorbent in soil, only a slight increase in sorption was observed as compared to the unamended soil, a 1.4-fold increase for Kd value and 1.7-fold increase for Kf (Table 2). OOW has been observed to increase diuron, another phenylurea herbicide, sorption *(13,21,33)*. While OOW is considered a good amendment for soils because of the increase in the soil organic matter content, this amendment´s impact on fluometuron sorption is lower as compared to biochars (except for BC2), and to diuron. In case of diuron sorption, the percentage of amendment used was 5-10% *(13,21,33)*, instead of the 2% used in this study. Baskaran and Kennedy *(4)* and Gámiz et al. *(26)* reported higher sorption of diuron than fluometuron on soil and organoclays, respectively under same experimental conditions, due to

higher water solubility of fluometuron as compared to diuron. As in the case of BC2, the high content in DOC of OOW should also contribute to this low sorption.

Fluometuron desorption was hysteretic for all samples ($1/nf_{des} < 1/nf_{ads}$) (Table 2), which means it is very difficult to desorb a significative amount of the sorbed herbicide and that desorption cannot be predicted accurately from sorption isotherms *(34)*. Irreversibility of the sorption process increased with the addition of biochar to soil, except for BC2 and OCl, as can be observed in the decrease of the hysteresis coefficient (H) (Table 2). The use of OOW as sorbent increased the reversibility of fluometuron sorption as compared to the non amended soil. In the case of organoclay *(35)* and OOW *(13)* the enhanced sorption is due to the combination of polar and hydrophobic interactions, which could favor the sorption reversibility.

MCPA

Sorption isotherms for MCPA for unamended and amended soils are shown in Figure 3, and, similarly to fluometuron, they can be divided into two adsorption levels: high-to medium, observed in the case of the soil amended with AC, BC5, OCl, and BC6; and, low sorption of MCPA in unamended soil and soil amended with BC1, BC2, BC3, BC4 and OOW, which all had nearly the same sorption. A small increase in MCPA sorption can be observed for amendment with BC4 and BC3 as compared to the unamended soil (Figure 3b). The isotherms were also L-type.

Sorption data fit the Freundlich equation for most amended soils (R^2 = 0.901-0.999) (Figure 3, Table 3). The R^2 criteria for the Freundlich equation was lower than the unamended soil and the soil amended with BC2 (0.704 and 0.784, respectively) and BC4 (R^2 = 0.470). MCPA Freundlich sorption coefficient in the unamended soil was Kf = 0.10 (Table 3), lower than values

reported in literature for MCPA 0.24-2.21 in unamended top soils with 0.18-4.61% OC content *(5,22)*.

Comparing Kd-15 values, sorption of MCPA on the unamended and amended soil was lower than fluometuron sorption, which is consistent with the octanol-water partition coefficient (log Kow; MCPA = -0.71, fluometuron = 2.28), as it has been reported for other herbicides' sorption *(23)*, revealing the role of hydrophobic sorbate-sorbent interactions. MCPA was completely adsorbed to the soil amended with the activated carbon as it was observed for fluometuron. According to Kd-15 values (Table 3), sorption of MCPA followed the trend S+BC5 > S+OCl > S+BC6 > S+BC4 > S+BC3 ≥ S+BC1 ≈ S+OOW > S > S+BC2, similar to fluometuron sorption, except for S+BC5, S+OCl, and S+BC2. Sorption of MCPA on the amended soils was correlated with the surface area of the amendment, as was observed for fluometuron. Activation of BC3 at 200 ºC for 2 hrs (BC4) slightly increased the sorption of the herbicide on the amended soil, as compared to the sorption on the soil amended with BC3. The effect of wheat ash on MCPA sorption was studied by Hiller et al. *(36)*, who observed a 10-to-15-fold increase in Kd values when a sandy and a sandy loam soil were amended with 1% of ash. These authors suggested that increase of MCPA sorption on the wheat ash amended soils was due to organic carbon content of the ash, and to the greater surface affinity for MCPA.

Amending the soil with BC2 decreased MCPA sorption on the soil, this effect was not observed for fluometuron and can be related association of DOM molecules from amendments and the anionic herbicide, as was observed by Cox et al. *(12)* for 2,4-D.

The incorporation of the HDTMA cation in the SAz1 clay provides a paraffinic structure to the clay, which creates a wide interlayer organic phase with high affinity for herbicides, and this is presumably the reason for the high sorption on S+OCl *(37)*. In the case of acids like 2,4-D, it has been shown that some polar interactions between ammonium groups of the alkylammonium and

carboxilic groups of the acid herbicide contributed to enhance the sorption *(38)*. The change in the trend of the sorption of MCPA on the soil amended with the organoclay as compared to BC5 could be attributed to the anionic character of the herbicide at pH of solution in equilibrium. MCPA sorption to the soil amended with OOW was similar to the sorption on the soil amended with the biochar produced from hardwood sawdust (BC1). Effect of OOW on MCPA sorption has been previously studied *(22)*, and an increase on MCPA sorption with the addition of olive mill waste to the soil was reported, which was attributed to the increase of OM from 1.6 to 4.3%. However, although in this study a 3-fold increase of the soil OM content with the OOW addition was observed, the final OM content of the soil amended was 1.36%, lower than the 4.3% reported in the previous study. The increase in sorption sites led by the increase in OM content would be counterbalanced by the association between the DOC and the herbicide molecules.

Desorption data of MCPA on the unamended soil and amended with the OCl, and BC3 fit to Freundlich equation ($R^2 > 0.9$), but the fit was worse on the soil amended with alperujo, BC2, and BC1 ($R^2 = 0.6$-0.89), and did not fit for the soil amended with BC6 and BC5 (Table 3). For MCPA desorption the hysteresis phenomenon was also observed, $1/nf_{des}$ values were lower than $1/nf_{ads}$ in all the cases.

Leaching studies

Fluometuron

Fluometuron was detected in all the leachates of the columns handpacked with the unamended soil and with the soils amended with all the sorbents on topsoil, except activated carbon. Breakthrough curves (BTCs) are shown in Figure 4, where two groups of curves can be observed: curves with low-to medium (maximum concentration of the herbicide leached 4-11%)

or no leaching of the herbicide (e. g. soils amended with AC, BC5, BC6 and OCl) or curves showing a high or complete leaching of fluometuron and maximum concentration peaks of fluometuron > 20% (unamended soil and soils amended with BC1, BC2, BC3, BC4, and OOW). Leaching of fluometuron in the unamended soil was complete (96 ± 5%) (Table 4). Potter et al. *(39)* reported a low run off of fluometuron on plots planted with cotton due to the fast leaching of the herbicide. Essington et al. *(3)* also observed 5-53% of the applied fluometuron leaching at a field site under natural rainfall conditions. Lower amounts of fluometuron were observed in the leachates of the soil amended with BC5, BC6, BC4, and OCl (Figure 4, Table 4), as compared to the unamended soil. This is in agreement with the higher sorption of fluometuron observed on the soils amended with those sorbents. Note that BC5 and BC6 are biochars with higher surface areas 46.0 and 16.2 m^2g^{-1}, respectively. Percent fluometuron leached was not affected by BC3, BC1, OOW, and BC2 used as sorbents, although the sorption study revealed higher sorption of the herbicide on the soils amended with these sorbents than on the unamended soil.

Lack of effect on fluometuron leaching with the addition of some biochars and OOW to the soil can be due to the content (Table 1) and interactions of dissolved organic carbon of the amendments with the herbicide, increasing its solubility and sorption reversibility, and enhancing its movement, as other authors have reported *(13,40,41)*. In the case of BC2, BC3, BC4, and BC6 the observed displacement of the peak maximum concentration to lower volumes (Figure 4a) could indicate some possible association of fluometuron with some components of DOC from these biochars *(41)*. This fact reveals the complexity and specificity of the processes involved in pesticide-soil-solution interactions in organically amended soils, primarily in cases of competition between DOC and herbicides for soil surfaces interactions sites, and even between soils surfaces and DOC for herbicides.

In Figure 4, a shift of the maximum concentration of fluometuron to larger pore volumes was observed only when OCl was used as sorbent. Gámiz et al. *(26)* reported a similar behavior of fluometuron leaching in a soil amended with a Na-rich Wyoming montmorrillonite modified with spermine cation. The strong and specific sorption exhibited by OCl for ureic herbicides *(35)*, enhances OCl+soil herbicide retention and hence delays leaching.

The total leaching of fluometuron in columns filled with the soil unamended and amended are shown in Figure 4b and they ranged from 0 to 100% and allow three different behaviors to be distinguished: 1) those amendments (OOW, BC1, BC2, and BC3) that slightly increased or decreased (BC4) the leaching with respect to unamended soil, 2) those amendments that largely decreased the amount of fluometuron leached out (OCl, BC6, and BC5) and 3) active carbon that fully immobilized fluometuron in soils. The high porosity of AC may result in micropore adsorption, such as it is described by Pignatello and Xing *(42),* which is difficult to distinguish from chemisorptions and hence render bound residues. However, the low leaching in the cases of BC5, BC6 and OCl is probably due to some specific molecular interactions between herbicides and these sorbents. The enhanced retention in the case of BC5 and BC6 is probably due to interactions of DOC with soil surfaces, which in turn, acts as a “bridge” between the surface and fluometuron, increasing its retention *(43).* In the case of OCl, polar interactions between ammonium and carbonyl groups of similar herbicides have been shown.

MCPA

MCPA BTCs are shown in Figure 5, where 3 different types of curves can be observed: no leaching of the herbicide corresponding to the soil amended with the AC, low-to medium leaching of MCPA with 5-10% maximum concentration of the herbicide leached in the soil

amended with OCl, BC5 and BC6; and high leaching (maximum peak concentration > 30%) in the unamended soil and the soil amended with BC1, BC2, BC3, BC4, and OOW. Shift of the maximum concentration of MCPA to smaller pore volumes was observed when the soil was amended with BC6 (Figure 5a), and no changes in the position of the highest concentration was detected in the soil amended with the other sorbents as compared to the unamended soil. The amount of MCPA leached in the columns handpacked with the unamended soil was lower than fluometuron, despite the lower sorption observed for MCPA in the sorption-desorption study. MCPA is considered a high mobile herbicide, due to its high water solubility and low sorption to organic and inorganic components of the soil because of its negative charge and high polarity *(44)*.

Leaching of MCPA decreased when the soil was amended with the biochars BC6 and BC5 to a 51% of the amount of herbicide initially applied in both cases (Table 5). MCPA was not detected in the leachate from the soil amended with the activated carbon and only the 34% of the amount of MCPA applied was detected in the leachates from the soil amended with the OCl. However, leaching of MCPA increased as compared to the unamended soil when the biochars BC1, BC2, BC3, BC4 and the OOW were used as sorbents. Composition of dissolved organic matter influences the mobility of the herbicide MCPA. Haberhauer et al. *(45)* observed an increase on MCPA leaching with the addition of humic acids to the eluent, and retention of the herbicide when fulvic acids were added, and, as it was pointed for fluometuron, the content of DOC of the amendments and interactions with MCPA can be responsible for the increase of the herbicide leaching. In a previous study, the effect of organoclays and olive mill waste on MCPA leaching was studied *(22)*. The use of both amendments decreased the amount of MCPA detected in the leachates as compared to the blank. However, the opposite effect has been observed on leaching

of MCPA in the soil amended with the olive mill waste, which can be attributed to changes on composition of the waste.

A slight shift of the maximum leaching concentration to lower volumes in BTCs was observed for the soil amended with BC4, and was more notable in the soil amended with BC6 (Figure 5). This effect observed in the soil amended with BC6 can be due to an initial increase of MCPA mobility by the formation of MCPA and DOC complexes; however the amount of MCPA leached from this amended soil was lower than from the unamended soil because of the higher sorption capacity of the amendment.

After the leaching experiment MCPA was extracted from the soil columns portions. Extraction of the herbicide was negligible because leaching was high or in soils where leaching was low can be attributed to the fast degradation of the herbicide in soil, with half life values reported < 7 d *(27,46)* or to interactions of the biochars´ DOC with soil surface (BC5, BC6) or MCPA with the organic cations at external surface of the modified clay, increasing sorption of the herbicide.

Addition of biochar as agricultural soil amendment was thought to be an efficient strategy to reduce the mobility in soil and risk of water contamination of the herbicides fluometuron and MCPA. However, our results showed that although in most cases addition of biochar increased sorption of the herbicides as compared to the unamended soil, leaching of the herbicides could be either reduced or promoted. Origin and C content of the organic matter of the amendment play an important role on herbicides sorption and herbicide and DOC complexes formation have to be taken into account and reveals the complexity and specificity of the processes involved in pesticide-soil-solution interactions in organically amended soils. In our study, biochar was not preincubated in the soil. However, it has been reported *(40)* that, depending on the nature of the organic amendment and the soil surface, OM can change with residence time in soil, which can

affect the herbicide-soil amendment interactions. Future studies should be carried out to determine the effect of biochar aged in soil on herbicide sorption interactions. Biochar and surface area are other important parameters to be considered for the sorbent election. Our results showed that biochars with higher surface area favored higher sorption and lower leaching of the herbicides studied, similar to the effect of the use of the modified clay as soil amendment. OOW slightly increased the herbicides sorption as compared to the unamended soil, but also increased the leaching and reversibility due to its high DOC content. Therefore previous studies on the effect of soil amendments on sorption and leaching of herbicides or on properties and composition of the sorbents are highly recommended before their application to agricultural soils to avoid the risk of water pollution because of the possible increase in herbicide mobility.

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Note

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557 Table 1. Chemical and physical properties of the amendments

Amendment	Feedstock	Production Temperature (ºC)	pH	% C	SSA (m^2g^{-1})	%N	DOC ($mg\ L^{-1}$)
BC1	Hardwood Sawdust	500 (Fast pyrolysis)	8.0	61.8	6.2	0.3	118 ± 46
BC2	Macadmia nut shells	850 (Flash pyrolysis)	6.2	77.7	3.3	0.6	352 ± 29
BC3	Hardwood (oak/hickory)	540	6.6	73.3	8.0	0.3	64 ± 38
BC4	Hardwood (oak/hickory)	540 (+ Thermal activation 200 ºC 2 h)	6.8	43.9	5.9	0.7	31 ± 0.2
BC5	Wood pellets	> 500 (Slow pyrolysis) (< 2 mm particle size)	5.5	77.3	46	0.4	48 ± 1.5
BC6	Wood pellets	> 500 + H_2O_2 activation (> 2 mm particle size)	9.8	69.3	16	0.2	38 ± 0.5
AC	Bituminous coal	800 (+ steam activation)	6.7	94.9	979	1.3	3.0 ± 0.4
OCl	Organoclay	n/a	6.5	22.5	20	1.3	5.4 ± 0.8
OOW	Olive oil waste	n/a	5.8	53.2	17	1.2	341 ± 17

558 SSA: Specific Surface Area, DOC: Dissolved Organic Carbon, n/a: not applicable

559 The amendments were obtained from the following suppliers: BC1 = Dynamotive (CQuest^{TM});

560 BC2 = Biochar Brokers, BC3 = Cowboy Charcoal, BC4 = activated by the USDA-ARS, St. Paul,

561 MN, BC5 = Chip Energy, BC6 = activated by the USDA-ARS, St. Paul, MN, OCl = The Clays

562 Mineral Society (Purdue University), AC = Siemens (Aquacarb® 816), and OOW = IFAPA
563 Venta del Llano[1].

564 [1]Names are necessary to report factually on available data; however, the USDA neither
565 guarantees nor warrants the standard of the product, and the use of the name by USDA implies
566 no approval of the product to the exclusion of others that may also be suitable.

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Table 2. Sorption-desorption coefficients of fluometuron in the unamended soil and soil amended with different biochars, organoclay, olive mill waste, and activated carbon

Soils	Kf ($mg^{1-1/nf} L^{1/nf} kg^{-1}$)	1/nf	R^2	Kd-15 ($L\ kg^{-1}$)	Kf_{des} ($mg^{1-1/nf} L^{1/nf} kg^{-1}$)	$1/nf_{des}$	R^2	H
S	0.44 (0.40-0.49)	0.67 ± 0.06	0.979	0.18 (0.16-0.20)	1.1 (0.9-1.3)	0.36 ± 0.08	0.917	0.53
S+BC1	1.65 (1.53-1.78)	0.51 ± 0.05	0.977	0.44 (0.41-0.47)	7.3 (6.6-7.9)	0.02 ± 0.05	0.048	0.03
S+BC2	0.30 (0.28-0.33)	0.89 ± 0.05	0.990	0.22 (0.20-0.25)	1.2 (1.2-1.3)	0.46 ± 0.02	0.995	0.52
S+BC3	1.38 (1.29-1.47)	0.61 ± 0.04	0.988	0.48 (0.45-0.52)	6.2 (5.8-6.7)	0.11 ± 0.03	0.847	0.19
S+BC4	2.04 (1.75-2.38)	0.55 ± 0.10	0.917	0.61 (0.52-0.71)	7.0 (6.9-7.1)	0.04 ± 0.01	0.882	0.07
S+BC5	13.1 (11.8-14.5)	0.47 ± 0.05	0.973	3.07 (2.77-3.41)	26.9 (26.8-26.9)	0	0.770	0
S+BC6	5.58 (4.94-6.30)	0.47 ± 0.08	0.929	1.33 (1.18-1.50)	16.0 (15.8-16.2)	0.03 ± 0.01	0.902	0.06
S+AC	--	--	--	--	--	--	--	--
S+OCl	17.2 (14.1-21.1)	0.59 ± 0.10	0.925	5.60 (4.57-6.86)	28.3 (27.3-29.4)	0.32 ± 0.07	0.921	0.54
S+OOW	0.74 (0.71-0.76)	0.62 ± 0.02	0.997	0.26 (0.25-0.27)	1.6 (1.4-1.9)	0.38 ± 0.08	0.916	0.61

Table 3. Sorption-desorption coefficients of MCPA in the unamended soil and soil amended with different biochars, organoclay, olive mill waste, and activated carbon

Soils	Kf ($mg^{1-1/nf} L^{1/nf} kg^{-1}$)	1/nf	R^2	Kd-15 ($L\ kg^{-1}$)	Kf_{des} ($mg^{1-1/nf} L^{1/nf} kg^{-1}$)	$1/nf_{des}$	R^2	H
S	0.10 (0.07-0.14)	0.54 ± 0.18	0.704	0.03 (0.02-0.04)	2.0 (1.9-2.0)	0	0.995	0
S+BC1	0.12 (0.11-0.14)	0.76 ± 0.07	0.975	0.06 (0.06-0.07)	4.8 (3.1-7.3)	0	0.597	0
S+BC2	0.03 (0.02-0.05)	0.67 ± 0.24	0.784	0.01 (0.01-0.02)	4.7 (2.0-11)	0	0.707	0
S+BC3	0.29 (0.24-0.35)	0.52 ± 0.10	0.901	0.08 (0.07-0.10)	1. 9 (1.8-2.0)	0	0.936	0
S+BC4	0.75 (0.50-1.13)	0.38 ± 0.23	0.470	0.14 (0.09-0.21)	--	--	--	--
S+BC5	4.13 (3.70-4.60)	0.59 ± 0.07	0.960	1.36 (1.22-1.52)	18.8 (18.0-19.5)	0.01 ± 0.03	0.008	0.01
S+BC6	1.90 (1.71-2.11)	0.66 ± 0.07	0.970	0.75 (0.68-0.83)	10.8 (10.4-11.2)	0	0.099	0
S+AC	--	--	--	--	--	--	--	--
S+OCl	0.88 (0.86-0.89)	1.03 ± 0.01	0.999	0.94 (0.92-0.96)	1.0 (0.9-1.2)	0.94 ± 0.05	0.994	0.91
S+OOW	0.16 (0.15-0.18)	0.62 ± 0.04	0.989	0.06 (0.05-0.06)	3.0 (2.3-3.9)	0	0.760	0

Table 4. Percentage of fluometuron leached, extracted and recovered from the column leaching experiment.

Soil	% Leached	Peak max concentration (mg L^{-1})	% Extracted 0-5 cm	% Extracted 5-10 cm	% Extracted 10-15 cm	% Extracted 15-20 cm	% Total Extracted	% Total Recovered
S	95.7 ± 5.27	2.31 ± 0.26	--	--	--	--	--	95.7 ± 5.27
S+BC1	102 ± 1.07	3.08 ± 0.24	--	--	--	--	--	102 ± 1.07
S+BC2	109 ± 3.34	3.60 ± 0.13	--	--	--	--	--	109 ± 3.34
S+BC3	99.6 ± 1.29	2.57 ± 0.01	--	--	--	--	--	99.6 ± 1.29
S+BC4	85.1 ± 1.41	2.09 ± 0.04	13.4	0.8	0.6	0.5	15.3	100 ± 1.41
S+BCE5	17.9 ± 0.87	0.45 ± 0.01	52.1 ± 0.09	0.93 ± 0.26	--	--	53.0 ±0.17	70.9 ± 0.26
S+BC6	44.8 ± 0.79	1.05 ± 0.03	35.2	1.4	0.3	0.1	37	81.8 ± 0.79
S+AC	--	--	48.2 ± 0.23	--	--	--	48.2 ± 0.23	48.2 ± 0.23
S+OCl	55.6 ± 1.96	1.13 ± 0.14	18.7 ± 0.98	0.87 ± 0.12	1.06 ± 0.23	1.47 ± 0.04	22.1 ± 1.35	77.7 ± 2.33
S+OOW	106 ± 2.75	3.18 ± 0.30	--	--	--	--	--	106 ± 2.75

Table 5. Percentage of MCPA leached, extracted and recovered from the column leaching experiment.

Soil	% Leached	Peak max concentration (mg L^{-1})	% Extracted 0-5 cm	% Extracted 5-10 cm	% Extracted 10-15 cm	% Extracted 15-20 cm	% Total Extracted	% Total Recovered
S	78.7 ± 5.16	3.36 ± 0.71	--	--	--	--	--	78.7 ± 5.16
S+BC1	90.1 ± 4.44	4.75 ± 0.51	--	--	--	--	--	90.1 ± 4.44
S+BC2	93.1 ± 0.75	4.63 ± 0.35	--	--	--	--	--	93.1 ± 0.75
S+BC3	82.9 ± 5.78	3.70 ± 0.32	1.3 ± 0.3	--	--	--	1.3 ± 0.3	84.2 ± 6.08
S+BC4	94.0 ± 0.53	3.95 ± 0.58	--	--	--	--	--	94.0 ± 0.53
S+BC5	50.8 ± 2.28	2.06 ± 0.07	--	--	--	--	--	50.8 ± 2.28
S+BC6	51.0 ± 0.99	1.94 ± 0.29	8.5 ± 1.5	--	--	--	8.5 ± 1.5	59.5 ± 2.49
S+AC	--	--	--	--	--	--	--	--
S+OCl	34.4 ± 0.46	1.50 ± 0.06	--	--	--	--	--	34.4 ± 0.46
S+OOW	90.3 ± 0.39	4.24 ± 0.51	--	--	--	--	--	90.3 ± 0.39

Captions to figures

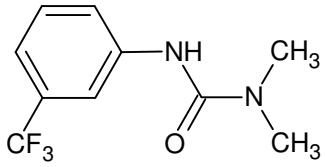
Figure 1. Chemical structure of the herbicides fluometuron and MCPA

Figure 2. a) Sorption isotherms of fluometuron on unamended soil and soil amended with biochars, organoclay, olive mill waste, and activated carbon. b) Sorption isotherms of fluometuron on unamended soil and amended with biochars and olive mill waste.

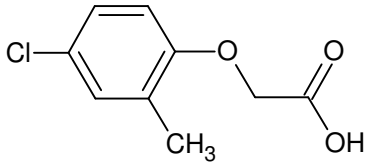
Figure 3. a) Sorption isotherms of MCPA on unamended soil and soil amended with biochars, organoclay, olive mill waste, and activated carbon. b) Sorption isotherms of MCPA on unamended soil and soil amended with biochars and olive mill waste.

Figure 4. a) Breakthrough curves (BTCs) of fluometuron leaching. b) Cumulative fluometuron leaching in the unamended and amended soil handpacked columns

Figure 5. a) Breakthrough curves (BTCs) of MCPA leaching. b) Cumulative MCPA leaching in the unamended and amended soil handpacked columns



Fluometuron



MCPA

Figure 1.

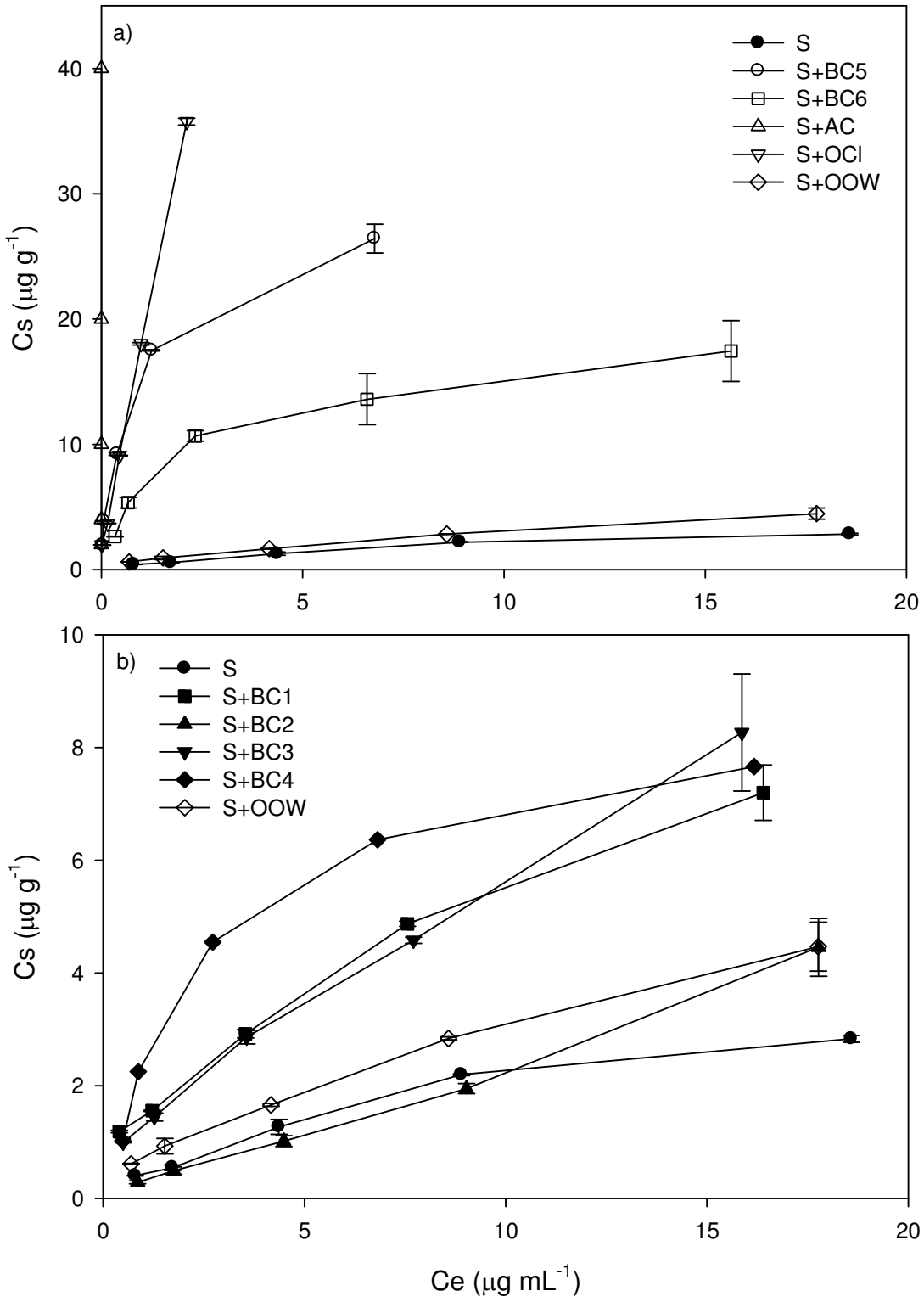

a)
S
S+BC5
S+BC6
S+AC
S+OCl
S+OOW
Cs (μg g-1)
0
10
20
30
40
0
5
10
15
20
b)
S
S+BC1
S+BC2
S+BC3
S+BC4
S+OOW
Cs (μg g-1)
0
2
4
6
8
10
0
5
10
15
20
Ce (μg mL-1)

Figure 2.

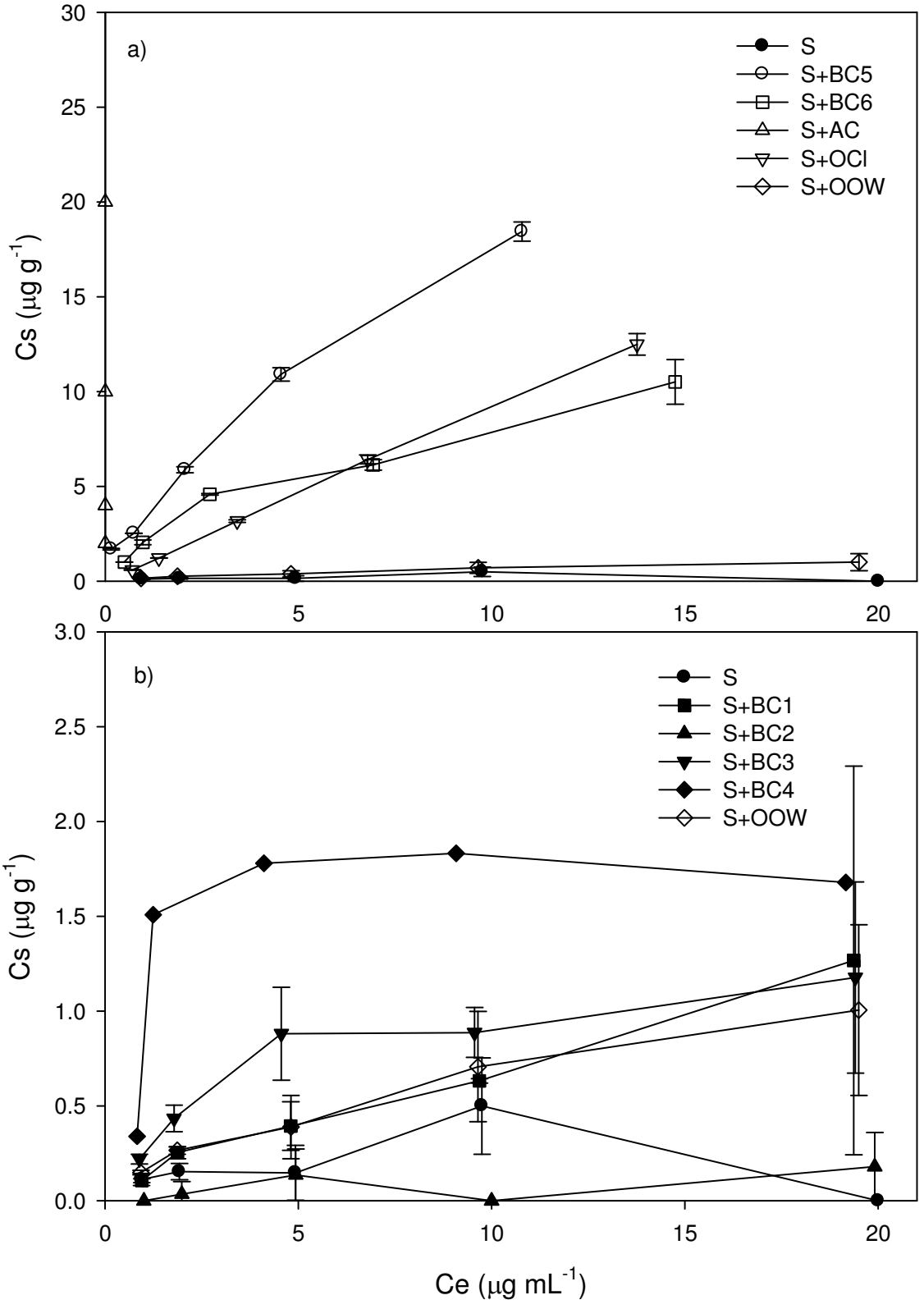

a)
S
S+BC5
S+BC6
S+AC
S+OCl
S+OOW
Cs (μg g-1)
b)
S
S+BC1
S+BC2
S+BC3
S+BC4
S+OOW
Cs (μg g-1)
Ce (μg mL-1)

Figure 3.

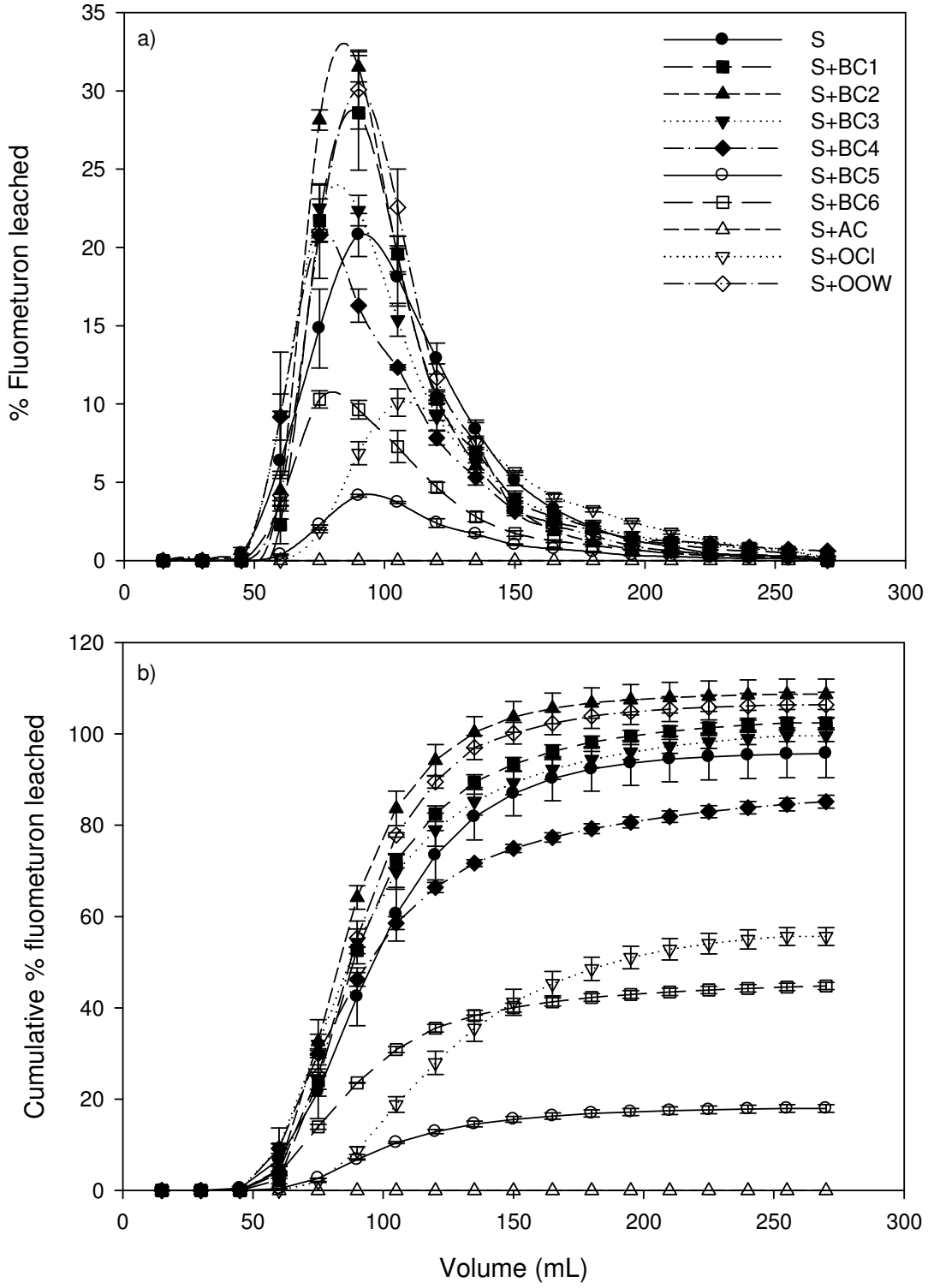

a)
% Fluometuron leached
S
S+BC1
S+BC2
S+BC3
S+BC4
S+BC5
S+BC6
S+AC
S+OCl
S+OOW
b)
Cumulative % fluometuron leached
Volume (mL)

Figure 4.

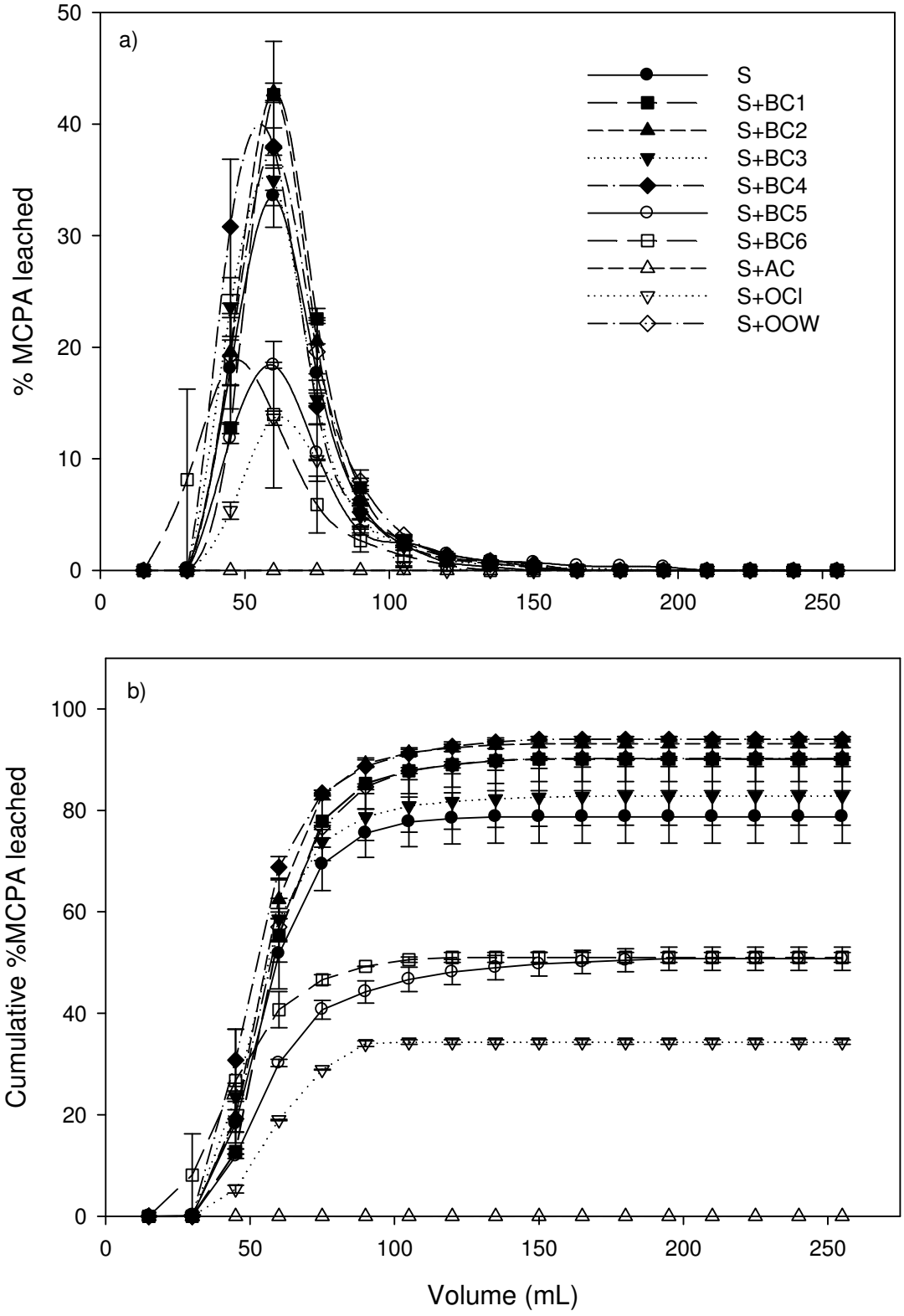

a)
% MCPA leached
S
S+BC1
S+BC2
S+BC3
S+BC4
S+BC5
S+BC6
S+AC
S+OCl
S+OOW
b)
Cumulative %MCPA leached
Volume (mL)

Figure 5.