Influence of biochar amendments on the sorption-desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil

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Highlights

- The effects of different biochars on the sorption of three pesticides on soil was evaluated
- Sorption of bentazone and aminocyclopyrachlor increased on the soils amended with the biochars with high SSA and low DOC content
- A very high sorption of pyraclostrobin was observed on the unamended and amended soils
- Desorption of the pesticides was hysteretic

Abstract

The many advantageous properties of biochar have led to the recent interest in the use of this carbonaceous material as a soil amendment. However, there are limited studies dealing with the effect of biochar on the behavior of pesticides applied to crops. The objective of this work was to determine the effect of various biochars on the sorption-desorption of the herbicides aminocyclopyrachlor (6-amino-5-chloro-2-cyclopropyl-4-pyrimidinacarboxylic acid), bentazone (3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide) and the fungicide pyraclostrobin (methyl 2-[1-(4-chlorophenyl) pyrazol-3-yloxymethil]-*N*-methoxycarbanilate) to a silt loam soil. Aminocyclopyrachlor and bentazone were almost completely sorbed by the soils amended with the biochars produced from wood pellets. However, lower sorption of the herbicides was observed in the soils amended with the biochar made from macadamia nut shells as compared to the unamended soil, which was attributed to the competition between dissolved organic carbon (DOC) from the biochar and the herbicides for sorption sites. Our results showed that pyraclostrobin is highly sorbed to soil, and the addition of biochars to soil did not further increase its sorption. Thus, addition of biochars to increase the retention of low mobility pesticides in soil appears to be not necessary. On the other hand, biochars with high surface areas and low DOC contents can increase the sorption of highly mobile pesticides in soil.

Keywords: Biochar, Fungicide, Herbicide, Organic amendment, Sorption

1. Introduction

The advantageous properties attributed to the use of biochar as soil amendment have favored the increase of its use and study. Among these properties is carbon sequestration, which refers to biochars' capability to prevent C from entering the atmospheric CO_2 pool by keeping it in a more stable C pool (Goldberg, 1985: Kuhlbusch & Krutzen, 1995; Lehmann et al., 2006). The high stability and resistance of biochar to degradation, as compared to the feedstock, allows this material to mitigate climate change through direct carbon sequestration (Lehmann, 2007; Lehmann et al., 2011), as well as potentially reducing soil greenhouse gas emissions (i.e. N_2O) following amendment (Ippolito et al., 2012; Spokas et al., 2009). Other benefits associated to biochar use are related to soil properties, such as its ability to decrease the soil bulk density (Laird, 2008; Sohi et al., 2010) and increase the soil water holding capacity (Tyron, 1948).

Biochar can also act as a fertilizer depending on feedstock type and can retain nutrients because of its high cation exchange capacity (CEC), which is related to the biochar surface area, negative surface charge and surface charge density (Liang et al., 2006). The availability of these retained plant nutrients could favor the increase in crop yields and productivity. However, some results reported have been contradictory (Spokas et al., 2012). Van Zwieten et al. (2010) studied the effect of two biochars produced from papermill waste on the biomass production of three plants species (wheat, soybean, and radish) on two soils types. When biochar was used without any additional fertilizer it increased only radish biomass production in both soils, and decreased wheat biomass in the calcarosol, but not in the ferrosol; no significant differences were reported for soybean biomass on either soil as compared to the control. The co-application of both biochar and fertilizer had a positive effect on biomass production in most plants studied, except wheat and radish in the calcarosol soil (Van

Zwieten et al., 2010). The existing studies indicate that the response of the soil system to biochar is dependent on both the soil and biochar properties.

The effect of biochar on pesticides applied to agricultural soils has received little study, although research dealing with this issue has increased in recent years. Among the processes involved in pesticides fate, sorption and dissipation has been the most studied (Cabrera Mesa and Spokas, 2011). There are recently published studies on the impact of biochar on sorption and dissipation of pesticides such as atrazine, terbuthylazine, diuron, isoproturon, and pyrimethanil (Cao et al., 2009; Martin et al., 2012; Sopeña et al., 2012; Spokas et al., 2009; Wang et al., 2010; Yu et al., 2010, 2006). An increase in pesticide sorption and decrease in dissipation were reported in these studies, which involved soils amended with fresh biochar. However, Martin et al. (2012) observed that biochars lose their sorptive capability over time with aging/weathering in the soil environment.

The effect of biochar on pesticide leaching has been reported in a few studies (Cabrera et al., 2011; Jones et al., 2011; Lü et al., 2012; Xu et al., 2012). In these studies, a decrease in pesticide mobility through the soil profile was observed upon amendment with biochar as compared to the control. However, in a previous study (Cabrera et al., 2011), three of six different biochars increased the leaching of the herbicide MCPA (4-chloro-2methylphenoxyacetic acid), and the addition of two of these biochars studied had no effect on mobility of fluometuron. The increase in leaching has been attributed to the lower specific surface area (SSA) and high DOC content of these biochars (Cabrera et al., 2011). These results clearly illustrate the effect of biochar properties on the observed impacts.

The objective of this research was to determine the effect of biochars made from different feedstocks and with different characteristics on the sorption-desorption of three chemical classes of pesticides, two of which are highly mobile herbicides and the third is a toxic fungicide. We also evaluated the efficacy of these biochars as soil amendments to reduce potential environmental pollution associated with the use of pesticides by increasing its sorption and reducing its mobility. The pesticides selected for this study were: i) bentazone, a post-emergence selective herbicide used to control broadleaf weeds in crops such as alfalfa, corn, rice, shorgum, and soybeans; ii) aminocyclopyrachor, approved for the control of broadleaf weeds, grasses, vines and woody species in non-crop, turf, sod farms and residential areas; and iii) pyraclostrobin, a strobilurin type fungicide with protectant, curative and translaminar properties, which is widely used in several different crops, including grape, cereals, citrus, potatoes, tomatoes and turf. Despite its links to naturally produced compounds in white rot fungi, pyraclostrobin is considered very toxic for aquatic organisms (Bringolf et al., 2007).

2. Materials and methods

2.1 Pesticides

Bentazone and pyraclostrobin (analytical grade and purity 99.9%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Aminocyclopyrachlor (^{14}C-labelled and pure analytical standards) was kindly supplied by DuPont (Wilmington, DE, USA). Chemical structures of the pesticides are shown in Figure 1 and physico-chemical characteristics in Table 1 (Data from Bukun et al., 2010; Du Pont, 2009 and the Pesticide Manual, 2006).

2.2 Soil

The soil used for the batch laboratory studies was collected from the University of Minnesota's Research and Outreach Station in Rosemount, MN (44°45' N, 93°04' W). Soil at the site is a Mollisol-Typic Hapludolls (USDA classification), containing approximately 22% sand, 55% silt, and 23% clay, pH 6.0 and organic carbon (OC) 2.52%. Surface soil (0-15 cm) was collected, sieved to < 2mm and homogenized for the study.

2.3 Biochars

Biochars produced from different feedstocks and under different conditions were used as soil amendments and compared to an activated charcoal (AC). The various biochar properties are summarized in Table 2. SSA of biochar was measured by nitrogen surface sorption, using a Carlo Erba Sorptomatic 1900 (Carlo Erba Instruments, Rodano, Italy) and the Brunauer, Emmett, and Teller (BET) method (Brunauer et al., 1983) on previously degassed 0.2 g of sample 80 ºC for 24 h. The pH was determined in a 1:5 biochar/deionized water slurry. Carbon and nitrogen contents were determined with ASTM method D5373-08. DOC from biochar was characterized according to Cox et al. (2004). Briefly, DOC was extracted with 0.01M $CaCl_2$ at 1:20 solid/solution ratio as duplicates. Suspensions were shaken for 15 minutes, centrifuged at 7083 g for 15 minutes, and filtered through a 0.45 μm pore glass fiber filter. DOC in the extracts was measured with a Shimadzu-V CSH analyzer (Shimadzu, Kyoto, Japan). Fluorescence absorption of the DOC of the extracts was measured at 254 nm with a Perkin Elmer Lambda EZ 210 UV-visible spectrophotometer (Perkin Elmer, Waltham, MA, USA). Extracts were diluted when absorption values were higher than 0.1 cm^{-1} to avoid matrix effects. Emission fluorescence from 300 to 480 nm of the extracts (adjusted pH = 2) and excited at 254 nm was determined in a F-2500-FL-Spectrophotometer by Hitachi (Tokyo, Japan) and the humification index was calculated as:

$$HIX = \frac{\sum_{WI=435}^{480} I}{\sum_{WI=300}^{345} I}$$

where *WI* is the wavelength in nanometers and *I* the fluorescence intensity at this wavelength (Cox et al., 2000; Zsolnay et al., 1999).

2.4 Sorption-desorption studies

2.4.1 Soil-solution ratio

Three soil:solution ratios (1:1, 1:3 and 1:8) were tested to select the appropriate ratio for the batch adsorption experiment. Five, 15 or 40 ml of bentazone solution 3 mg L^{-1} in 0.01M $CaCl_2$ or pyraclostrobin solution, 0.3 and 1 mg L^{-1} 0.01 M $CaCl_2$, was added to 5 g (dry weight) of soil placed in triplicate glass centrifuge tubes. The biochar was added at a rate of 10% (w/w) and mixed thoroughly. Tubes were shaken overnight and then centrifuged at 370 g for 20 min. An aliquot of the supernatant was filtered (0.45 µm, glass fiber) prior to analysis.

Samples were analyzed by HPLC using a Waters chromatograph with a 2996 Waters photodiode array detector (Waters Corporation, Milford, MA, USA) and a Zorbax SB-C18 column (4.6 × 150 mm, 5µm film thickness) (Agilent, Santa Clara, CA, USA). The mobile phase for bentazone was a gradient of water acidified with H_3PO_4 (pH=3) and acetonitrile starting at 50% acetonitrile and changing to 40% at 3 min, remaining constant for 2 minutes, then increasing to 50% acetonitrile at 6 min. Wavelength detection was set at 210 nm. For pyraclostrobin, the eluents of the mobile phase were the same as for bentazone and the gradient, which started at 70% acetonitrile, changed to 100% at minute 3, remaining constant for 3 minutes and changed to the initial conditions at minute 8. Wavelength detection was set at 277 nm. For both pesticides the flow rate was 1 mL min^{-1}, and the injection volume 50 µL.

Percentage of pesticide adsorbed on the unamended or amended soil was calculated as: %Ads = [(C_i - C_e)/C_i] x 100. Sorption coefficient K_d was also calculated with the equation K_d = C_s/C_e, being C_s the amount of herbicide sorbed on the unamended or amended soil (C_i - C_e) × V/M, being C_i the pesticide initial concentration, C_e the equilibrium concentration, V the volume of pesticide solution added and M the soil mass.

2.4.2 Batch sorption

Batch sorption was performed according to OECD guideline 106 (OECD, 2000). Duplicate samples (5 g) of unamended and 10% (w/w) biochar amended soils were treated with 5 ml of bentazone and aminocyclopyrachlor solutions (initial concentrations, C_i= 0.03, 0.1, 0.3 and 1 mg L^{-1} in 0.01 M $CaCl_2$ for bentazone and 0.01, 0.03, 0.1 and 0.3 mg L^{-1} for aminocyclopyrachlor in 0.01M $CaCl_2$ and 108 Bq ml^{-1} radioactivity) or 40 ml of pyraclostrobin solution (initial concentrations, C_i= 0.03, 0.1, 0.3 and 1 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 (Boivin et al., 2005; Oliveira et al., 2011). Samples were shaken for 24 h and centrifuged at 370 g for 20 min. Equilibrium concentrations (C_e) in the supernatants after 24 h of equilibration time were determined by HPLC for bentazone and pyraclostrobin as previously described. Aminocyclopyrachlor concentration was determined by liquid scintillation counting (Oliveira et al., 2011); briefly, 1 ml aliquot was mixed with 5 ml of scintillation cocktail and counted for 5 min in a Tri-Carb 1500 Packard liquid scintillation counter (Packard Instrument Company Inc. Meriden, CT, USA).

Differences between C_i and C_e were assumed to be the amounts of chemical adsorbed (C_s). Sorption isotherms were fitted to the Freundlich equation, $C_s = K_f \cdot C_e^{1/nf}$, and adsorption coefficients (K_f) and slope isotherms ($1/n_f$) were calculated. In cases of different $1/n_f$ values, K_f data cannot be compared. Therefore, $K_{d-0.05}$ was determined as C_s/C_e , being C_e=0.05 mg L^{-1}, an intermediate value of the concentrations studied in the batch sorption.

Herbicide desorption was performed by successive 24-h equilibrations of soil (three times) with 0.01 M $CaCl_2$ using the soil that was initially equilibrated with the maximum initial pesticide concentration, 1 mg L^{-1} for bentazone and pyraclostrobin and 0.3 mg L^{-1} for aminocyclopyrachlor. Hysteresis coefficient was determined as $H = 1/n_{fdes} / 1/n_{fads}$ (Barriuso et al., 1994; O´Connor et al., 1980).

3. Results and discussion

3.1 Characterization of the biochars

As shown in Table 2, the pH values for the biochars ranged from 6.2 to 10.8, total carbon ranged from 69 to 94% and nitrogen content from 0.3 to 1.3%. The untreated biochars had the lowest SSA (3.3 to 29 m^2 g^{-1}), whereas the AC possessed a surface area of 979 m^2g^{-1}. Biochar made with macadamia nut shells (BC18, Table 2) had the highest measured DOC, and AC had the lowest DOC content. Maximal fluorescence intensity of DOC from the biochars appeared at wavelength ≈ 390-400 nm (Figure 2). Fluorescence was a maximum in the region of 300 nm for the less condensed and non-humified material, and in the region of ≥ 400 nm wavelengths for condensed molecules, presumably aromatic and typical for humic materials (Cox et al., 2004, Zsolnay et al., 1999). We did not observe great differences in the HIX calculated for the different biochars. However, HIX values were slightly lower for BC18 and BC29 than for CE3 and BC15, which indicates BC18 and BC29 biochars potentially have greater amounts of non-humified material (i.e. non-charred original biomass).

3.2 Soil solution ratio

The soil:solution ratio selected for the sorption study of bentazone was 1:1. The amount of herbicide sorbed on the unamended soil was 27% of the initial solution of 3 mg L^{-1} when the ratio 1:1 was used, and decreased to 3% when the ratio was 1:8. Sorption of bentazone in the soil amended with BC18, BC29 and CE3 ranged from 21 to 95% in a case of 1:1 ratio, from 11 to 93% for 1:3 ratio, and from 6 to 36% for 1:8 ratio.

The fungicide pyraclostrobin was completely sorbed on the unamended soil at the 3 ratios studied when the intial concentration was 0.3 mg L^{-1}, and 97, 92 and 78% of the initial solution 1 mg L^{-1} was adsorbed at ratios 1:1, 1:3 and 1:8, respectively. Sorption of the fungicide ranged from 78 to 83% on the biochar amended soils at ratio 1:3 and from 82 to 85% at the 1:8 ratio. According to these results the ratio of 1:8 was selected for the sorption-desorption studies of pyraclostrobin and sorption-desorption of aminocyclopyrachlor was studied at a ratio of soil to solution 1:1.

3.3 Sorption-desorption isotherms

3.3.1 Bentazone

Bentazone was completely sorbed on the soil amended with the biochars CE3, BC15 and AC, and thus bentazone sorption Freundlich coefficients could not be determined for these amended soils. Sorption data of bentazone on the unamended soil and the soil amended with BC18 and BC29 fitted the Freundlich equation ($R^2 \geq 0.88$) as shown in Table 3. The isotherm corresponding to the unamended soil was linear ($1/n_f = 1.1$, Table 3), which indicates a constant partition of solute between solution and substrate (Giles et al., 1960). A decrease in the linearity of sorption isotherms with the addition of biochar has been reported for several pesticides (Martin et al., 2012; Yu et al., 2010). The slope mean values of the bentazone isotherms are lower for the biochar amended soils than for the unamended soil, but considering the error values, no significant differences can be concluded from these data. Only in the case of the soil amended with BC18 was the slope of the isotherm lower than unity, indicating a high dependence of sorption on intial solution concentration, with proportionally higher sorption at lower concentration as compared to higher ones.

Bentazone K_f value calculated for the unamended soil (0.9 $mg^{1-1/nf}$ $L^{1/nf}$ kg^{-1}) is in general agreement with results reported by Li et al. (2003) 0.14-0.48 $mg^{1-1/nf}$ $L^{1/nf}$ kg^{-1} in five soils and by Boivin et al. (2005) 1.2-1.9 $mg^{1-1/nf}$ $L^{1/nf}$ kg^{-1} in thirteen contrasting soils. Sorption of bentazone on the amended soils is related to the SSA and DOC content of the biochars. Bentazone was sorbed to a lesser extent on the soils amended with the biochars with higher content of DOC. These biochars also have lower HIX values, indicating that the less condensed and non-humified portion predominately contributes to its DOC fraction. More importantly, this DOC can be sorbed to soil particles and thereby competing with the herbicide for sorption sites (Cox et al., 2000). Due to the anionic character of the herbicide, this effect can be also attributed to repulsion between negatively charged bentazone molecules and COO^- groups of the biochar, as it was observed by Cox et al. (2000) on the sorption of another acid herbicide (2,4-D) in a soil treated with a commercial humic amendment. Although there is a considerable amount of DOC present on the CE3 biochar, bentazone was completely sorbed on the soil amended with this biochar, indicating the important role of SSA in herbicide sorption. Other authors have also related the increase on sorption of pesticides with the increase of the SSA of the biochars added to soils (Uchimiya et al., 2012; Yu et al., 2010).

3.3.2 Pyraclostrobin

Pyraclostrobin was highly sorbed in the unamended soil. Data fit the Freundlich equation ($R^2 = 1$) (Table 3), and had a slope > 1, indicating that fungicide and water molecules are in competition for sorption sites (Giles et al., 1960). Our results were in agreement with pyraclostrobin sorption values found in literature (K_d: 30-360 ml g^{-1}), which also indicate that the fungicide is strongly retained by soil components (FAO/WHO, 2005). Addition of biochar to the soil led to complete sorption of the fungicide and did not allow determination of the Freundlich coefficients. Due to the high sorption of pyraclostrobin on soil reported in literature and observed in this study, there is low risk for this fungicide to leach to groundwater or to move in the soil. Therefore, pyraclostrobin can be considered a non-mobile pesticide. Thus, there is no reason to use biochar or any other soil organic amendment to increase pyraclostrobin sorption to reduce the risk of offsite transport and water contamination.

3.3.3 Aminocyclopyrachlor

Sorption data of the herbicide fit the Freundlich equation ($R^2 \geq 0.97$) and the resulting values are shown in Table 3. The K_f value calculated for the herbicide sorption on the unamended soil (1.02 $mg^{1-1/nf}$ $L^{1/nf}$ kg^{-1}) is in agreement with the data reported by Oliveira et al., (2011) (0.06 to 1.16 $\mu mol^{1-1/nf}$ $L^{1/nf}$ kg^{-1}), for aminocyclopyrachlor sorption on 14 Brazilian soils. Slopes of the isotherms were close to one, which indicates that herbicide sorption is mainly a partitioning mechanism between solid organic matter and solution, without any apparent limits to the sorption (Giles et al., 1960), except in the case of the soil amended with AC, where slope was greater than one.

Aminocyclopyrachlor sorption increased in the soil amended with the biochars CE3 and BC15, which have greater SSA, HIX, and lower DOC content. However, sorption of the herbicide in the soil amended with the biochars BC18 and BC29 with lower SSA and higher DOC contents was even lower than in the unamended soil. Sorption of aminocyclopyrachlor on the unamended and amended soils followed the trend: S+AC >>> S+BC15 > S+CE3 $\geq$ S > S+BC29 $\approx$ S+BC18. The difference in the sorption behavior between the biochars and activated charcoal was statistically significant ($p < 0.05$; Student´s t test). The lower HIX values indicate that DOC is constituted by small molecules and less humified than in the case of higher HIX values (Cox et al., 2000). The lack of effect of the biochar on aminocyclopyrachlor sorption, or even the decrease in sorption can be related to interactions of biochar DOC molecules and the mineral soil surfaces, resulting in competition with the herbicide for the same mineral sorption sites (Cox et al., 2004) or to displacement of weakly sorbed aminocyclopyrachlor.

3.3.4 Desorption

Desorption was hysteretic for all pesticides on all samples ($1/n_{f\ des} < 1/n_{f\ ads}$) (Tables 3 and 4), which according to Koskinen et al. (2006) means that it is difficult to desorb the pesticide previously sorbed, and desorption cannot be predicted accurately from sorption isotherms. No desorption of aminocyclopyrachlor occurred in the soil amended with the AC and was almost negligible from the soil amended with the BC15 as can be seen by the low H value (Table 4). Reversibility of bentazone and aminocyclopyrachlor sorption increased in the soils amended with BC18 and BC29, where H was higher than in the unamended soil and is in accordance with the lower observed sorption. Unlike sorption, there was no statiscally significant difference between the biochars and the activated charcoal for aminocyclopyrachlor desorption ($p > 0.05$; Student´s t test).

4. Conclusions

While potentially beneficial for many reasons, the use of biochar as soil organic amendment does not always ensure greater pesticide sorption. The source and amount of organic matter on the biochar can alter pesticide sorption and these effects can be different for different types of pesticides. According to our results, biochars with not only high values of SSA, but also low DOC content and high HIX values increase the sorption and decrease the sorption reversibility of pesticides on soil as compared to the non-amended soil. However, in the case of using biochars with lower SSA and HIX and higher DOC content, pesticide sorption can be even lower than in the unamended soil. In conclusion, characterization of biochar to be used as a soil amendment is highly recommended prior to field application to optimize sorption conditions and to prevent increased soil and water pesticide contamination following biochar application.

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Table 1. Physico-chemical characteristics of the pesticides used

Pesticide	Molecular Weight (g mol^{-1})	Solubility in water (pH 7, 20ºC) (mg L^{-1})	K_{ow} (log P) (pH 7, 20ºC)	pK_a
Aminocyclopyrachlor	213.6	4200	-2.48	4.7
Bentazone	240.3	570	-0.46	3.3
Pyraclostrobin	387.8	1.9	3.99	--

Table 2. Physico-chemical properties of the biochars

Biochar[a]	Feedstock	Production T (ºC)	C (%)	N (%)	pH	SSA[b] (m^2 g^{-1})	DOC[c] (mg L^{-1})	HIX[d]
CE3	Wood chips pellets	> 500 (Slow pyrolysis)	73.9	0.4	10.8	28.8	52 ± 1[e]	1.89
BC15	Wood chips pellets	> 500 (Slow pyrolysis)	69.3	0.2	9.8	17.8	14 ± 0	1.55
BC18	Macadamia nut shells	850 (Flash pyrolysis)	77.7	0.6	6.2	3.3	352 ± 29	1.39
BC29	Hardwood (oak/hickory)	540	73.3	0.3	6.6	8.0	64 ± 38	1.31
AC	Bituminous coal	800 (+ steam activation)	94.9	1.3	6.7	979	3 ± 0	0.90

[a] Adsorbents manufacturers: CE3 and BC15 Chip Energy Inc. Goodfield, IL, USA, BC18 Biochar Brokers, Denver, CO, USA, BC29 Cowboy Charcoal LLC, Pall Mall, TN, USA, AC Siemens Water Technology Corp. Alpharetta, GA, USA. [b] SSA: Specific surface area. [c] DOC: Dissolved organic carbon. [d] HIX: Humification index. [e] Mean ±standard error, n=2.

Table 3. Freundlich sorption coefficients (K_f) and sorption coefficients at C_e= 0.05 mg L^{-1} ($K_{d-0.05}$) for the pesticides in the unamended soil and soil amended with biochars

Pesticide	Sample	K_f ($mg^{1-1/nf}$ $L^{1/nf}$ kg^{-1})	$1/n_f$	R^2	$K_{d-0.05}$ (L kg^{-1})
Bentazone	S	0.90 (0.42-1.81)[a]	1.09 ± 0.34[b]	0.91	0.70 (0.32-1.40)[a]
	S+BC18	0.48 (0.39-0.60)	0.74 ± 0.11	0.98	1.04 (0.84-1.29)
	S+BC29	0.92 (0.46-1.85)	0.84 ± 0.31	0.88	1.47 (0.73-2.96)
Pyraclostrobin	S	101	1.59	1.00	17.25
Aminocyclopyrachlor	S	1.02 (0.98-1.07)	0.96 ± 0.01	1.00	1.14 (1.09-1.20)
	S+CE3	1.89 (1.08-3.30)	0.97 ± 0.13	0.97	2.09 (1.19-3.64)
	S+BC15	25.4 (11.5-56.0)	0.96 ± 0.12	0.97	28.9 (13.1- 63.8)
	S+BC18	0.62 (0.53-0.73)	0.98 ± 0.05	1.00	0.66 (0.56-0.77)
	S+BC29	0.71 (0.66-0.77)	0.93 ± 0.02	1.00	0.87 (0.81-0.95)
	S+AC	18880 (5280-67515)	1.31 ± 0.13	0.98	7526 (2104-26914)

S:Rosemount Soil, AC: Activated Carbon, [a] Numbers in parenthesis are standard errors about the mean, n=2 , [b] Numbers are mean ± standard errors.

Table 4. Freundlich desorption coefficients ($K_{f\ des}$) and hysteresis coefficients (H) for the pesticides in unamended soil and soil amended with biochars

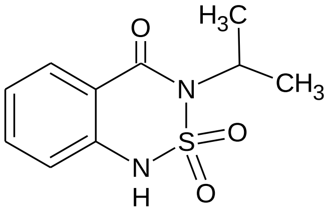
Pesticide	Sample	$K_{f\ des}$ ($mg^{1-1/nf}$ $L^{1/nf}$ kg^{-1})	$1/n_{f\ des}$	R^2	H
Bentazone	S	0.44 (0.42-0.45)[a]	0.08 ± 0.02[b]	0.89	0.08
	S+BC18	0.42 (0.39-0.46)	0.38 ± 0.07	0.94	0.52
	S+BC29	0.51 (0.48-0.54)	0.12 ± 0.04	0.83	0.15
Pyraclostrobin	S	9.11 (8.06-10.30)	0.06 ± 0.05	0.37	0.04
Aminocyclopyrachlor	S	0.44 (0.40-0.50)	0.54 ± 0.05	0.98	0.56
	S+CE3	0.32 (0.30-0.34)	0.25 ± 0.02	0.98	0.26
	S+BC15	0.29 (0.28-030)	0.01 ± 0.01	0.31	0.01
	S+BC18	0.35 (0.34-0.36)	0.70 ± 0.01	1.00	0.71
	S+BC29	0.43 (0.41-0.45)	0.67 ± 0.02	1.00	0.72
	S+AC	0.298 (0.297-0.299)	0	0.65	0

S:Rosemount Soil, AC: Activated Carbon, [a] Numbers in parenthesis are standard errors about the mean, n=2 , [b] Numbers are mean ± standard errors.

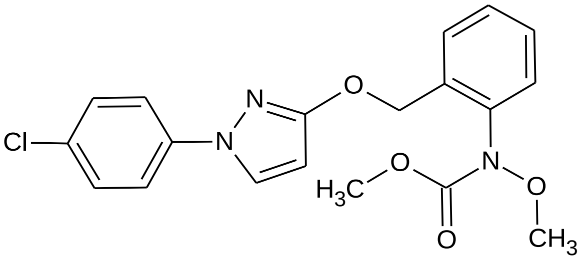
Caption to Figures

Figure 1. Chemical structure of the pesticides

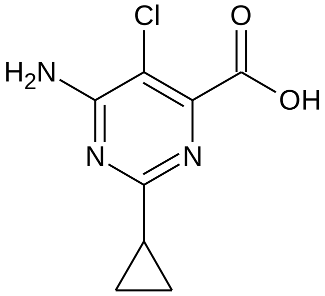
Figure 2. Emission fluorescence spectra of the DOM extracted from the biochars and AC. a) Intensity measured. b) Intensity normalized to the maximum intensity measured.



Bentazone

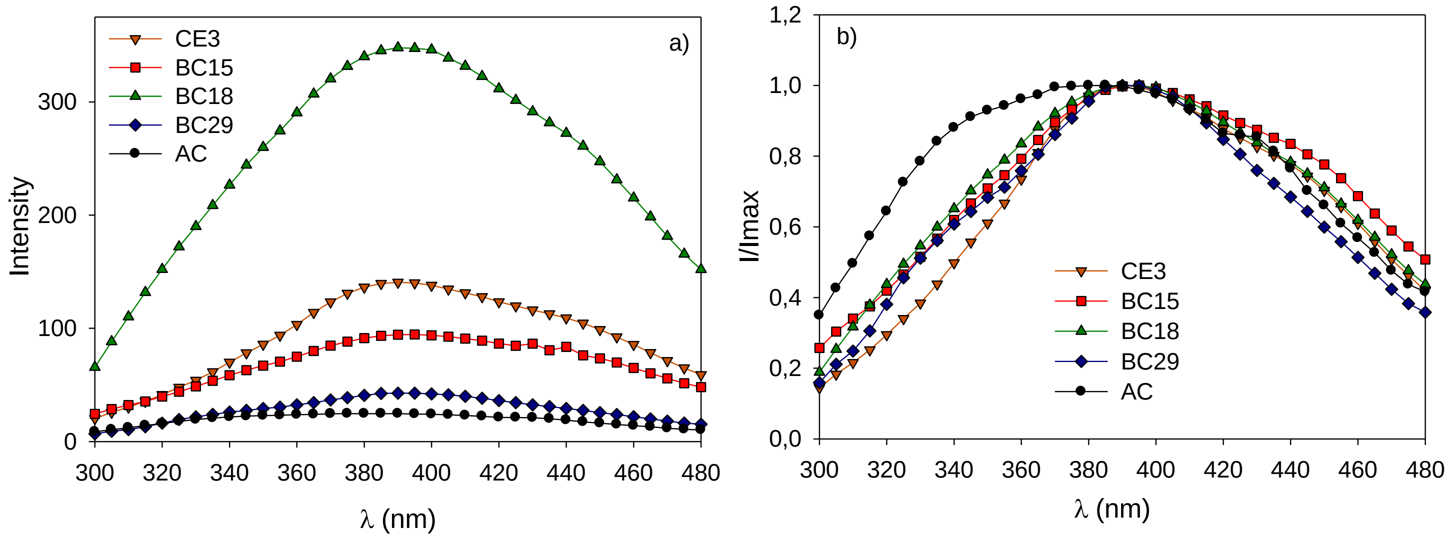


Pyraclostrobin



Aminocyclopyrachlor

Figure 1.



a)
Intensity
300
200
100
0
300
320
340
360
380
400
420
440
460
480
λ (nm)
CE3
BC15
BC18
BC29
AC
b)
I/Imax
1,2
1,0
0,8
0,6
0,4
0,2
0,0
300
320
340
360
380
400
420
440
460
480
λ (nm)
CE3
BC15
BC18
BC29
AC

Figure 2.

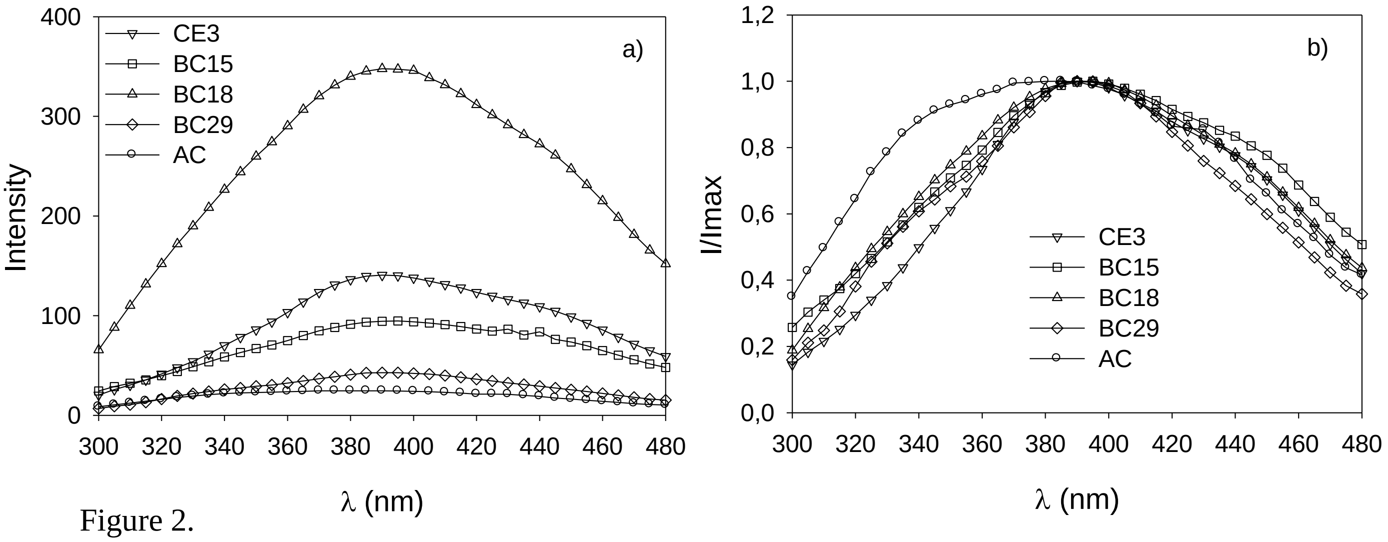

a)
Intensity
0
100
200
300
400
300
320
340
360
380
400
420
440
460
480
λ (nm)
CE3
BC15
BC18
BC29
AC
b)
I/Imax
0,0
0,2
0,4
0,6
0,8
1,0
1,2
300
320
340
360
380
400
420
440
460
480
λ (nm)
CE3
BC15
BC18
BC29
AC

Figure 2.