Influence of Wheat Ash on the MCPA Immobilization in Agricultural Soils

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Sorption-desorption behavior of MCPA and other anionic herbicides in soils influences their persistence and bioefficacy and is the major determinant of their mobility in various compartments of environment (Guo et al., 2000; Jensen et al., 2004; Socías-Viciana et al., 1999). The sorption and desorption characteristics of anionic herbicides are dependent on the soil properties, such as soil organic carbon content, soil pH and the properties of the herbicide (Bekbölet et al., 1999; Haberhauer et al., 2000). However, recent studies have shown that soil ashes may significantly contribute to the herbicide sorption in soils (Chiou et al., 2000; Yang and Sheng, 2003; Zhang et al., 2004). The burning of crop residues in the fields is a routine post-harvest practice and results in a direct accumulation of ashes in soils. The ashes usually contain high-surface-area carbonaceous materials due to combustive carbonization. Many studies have suggested that high-surface-area carbonaceous materials are responsible for the high sorptivity of neutral organic chemicals in soils and sediments in a fashion similar to that of activated carbon (Allen-King et al., 2002; Cornelissen et al., 2005). However, influence

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of crop-residue-derived ashes on sorption- desorption behavior of anionic herbicides in soils has been much less studied (Sheng et al., 2005). Taking into account the above and the fact that the burning of crop residues in the field is a common agricultural practice in Slovakia, the objective of this study was to investigate MCPA sorption-desorption in two different soils from Slovakia containing crop-residue-derived ashes. This study was conducted to evaluate the potential role of ashes in MCPA immobilization in soils.

Materials and Methods

Analytical grade MCPA ((4-chloro-2-methylphenoxy)acetic acid) (purchased from Dr Ehrenstorfer GmbH) with 825 mg.L^{-1} water solubility at 25°C and pK_a = 3.07 was used. MCPA is mostly neutral at pHs < 3.07 and becomes deprotonated (negatively charged) at pHs > 3.07. Primary stock solution of MCPA was prepared by dissolving it in a background solution consisting of deionized and sterilized water (Milli Q+), 10^{-4} M NaN$_3$ to prevent biological activity and 0.01 M CaCl$_2$ to keep ionic strength constant.

Wheat (*Triticum aestivum* L.) residue was used in this study. Air-dried residue (1 kg) was burned on a steel plate (50 × 40 cm) in a garden under natural conditions at the end of April. Burning of 1 kg of air-dried wheat residue produced 48 g of wheat ash. The ash contained 11.8% elemental carbon and 21.0% silicon. The specific surface area of the ash was not measured. However, Yang and Sheng (2003) reported that the specific surface area of the wheat ash was 10.1 m^2.g^{-1}. The pH measured in suspension of ash was 10.7. The ash was used either pure or mixed with soils.

Two surface soils (0-30 cm) were collected from cultivated fields of Western Slovakia. One soil was Arenic

Fluvi-Gleyic Phaeozem (labelled as soil I in the text) collected from a field near Stupava (15 km northerly from Bratislava). A second soil was Eutric Regosol (labelled as soil II in the text) collected from a field near Lozorno (30 km northerly from Bratislava). The composition and physico-chemical characteristics of the two soils are given in Table 1. The soil samples were air-dried, crushed and sieved through a 2 mm mesh. Ash-amended soils (1.0% ash) were prepared by thoroughly mixing wheat ash with soils in a ratio of 1:99 (by weight).

Sorption isotherms for MCPA in pure soils, pure wheat ash and ash-amended soils were obtained by a batch equilibration technique. A predetermined weight of each sorbent (2 g of pure soil, 0.25 g of ash-amended soils, and 0.05 g of pure ash) and 10 mL of 0.01 M calcium chloride solution containing various amounts of MCPA were mixed in a series of 15 mL glass centrifuge tubes. Five initial MCPA concentrations ranging from 1.66 to 56.6 mg.L^{-1} were used. The glass centrifuge tubes were shaken automatically for 24 hr. At the end of the shaking period, sorbents and aqueous phases were separated by centrifugation at 3000 rpm for 10-15 min. The MCPA concentrations in supernatants were analyzed by a reversed-phase high-performance liquid chromatography (Hewlett-Packard model 1100, 5 μm, 4.6 × 125 mm LICHRO-SPHERE-100 RP column) fitted with a fluorescence detector (Hewlett-Packard 1046A). External solution standards were used to establish linear calibration curves for a fluorescence detector. The mobile phase used was a mixture of acetonitrile and 0.05 M phosphate acid solution. The flow rate of this mobile phase was kept at the level of 0.4 mL.min^{-1}. The average uncertainty for the measured concentrations was about ±10%, and the detection limit for the aqueous extracts was 0.02 mg.L^{-1}. The amount of MCPA sorbed was calculated by the difference between the amount initially added and that remaining in the equilibrium solution. Control samples containing only MCPA solution without sorbent were subjected to the same steps as the test system, in order to check MCPA stability and possible adsorption onto the surface of the tubes. No losses of MCPA due to adsorption onto the surface of the tubes or volatilization were observed. Sorption tests for MCPA-pure soil combinations were made in duplicate. Measurements with ash-amended soils and pure ash were made in triplicate.

Desorption was determined on the same samples used for the sorption test with an initial MCPA concentration of 56.6 mg.L^{-1}. The supernatants were carefully removed (~ 9 mL for pure soils and 9.9 mL for pure ash and ash-amended soils). MCPA-free 0.01 M calcium chloride solution in the same amount as removed was added to the tubes to bring the volume back to the original. The tubes were shaken for 24 hr. At 24 hr, duplicate or triplicate tubes were centrifuged, and the supernatants were analyzed for MCPA concentrations as described above.

Results and Discussion

Figure 1 shows the sorption isotherms of MCPA in pure soils, ash-amended soils and pure wheat ash. Sorption of MCPA by the pure soils displayed a nonlinear isotherm. The nonlinear sorption isotherms for MCPA and similar anionic herbicides have been frequently reported (Bekbölet et al., 1999; Socías-Viciana et al., 1999; Thorstensen et al., 2001), and this might be explained by an increased difficulty to access the active sorption sites when pesticide concentrations in solution are elevated. The sorption of MCPA by the soil I appeared to be slightly higher than that by soil II. The sorption difference may be indicated by the sorption coefficient (K_d), calculated by dividing the amount sorbed by the corresponding equilibrium concentration. For example, at the equilibrium concentration of approximately 1.50 mg.L^{-1}, the sorption coefficients were 1.10 L.kg^{-1} and 0.36 L.kg^{-1} for the soil I and II, respectively. The higher sorption of MCPA by soil I over soil II can be attributed to the higher organic carbon content of the former soil, which is consistent with frequently observed positive correlations between sorption of anionic herbicides and soil organic carbon content (Bekbölet et al., 1999; Boivin et al., 2005). Generally, MCPA sorption by the two soils was low, indicating that MCPA is a potentially mobile herbicide in soils.

Sorption of MCPA by wheat ash displayed the characteristics of the Langmuir adsorption isotherm (Fig. 1c), suggestive of the surface adsorption of MCPA by the ash. The isotherm of the Langmuir-type for MCPA sorption by wheat ash observed in this study was similar to those earlier reported for adsorption of 2,4-D and MCPA by activated carbons (Aksu and Kabasakal, 2004; Nyazi et al,. 2005). The similarity indicates that wheat-residue-derived

Table 1 Selected physico-chemical characteristics of the soils used

Sample	Clay(%)	Silt(%)	Sand(%)	Texture	pH$_{H2O}$	OC[1](%)	Main clay minerals
Soil I	11	15	74	sandy loam	7.96	1.19	Ill > Chl[2]
Soil II	0.6	13.9	85.5	sandy	5.76	0.48	Ill > Chl

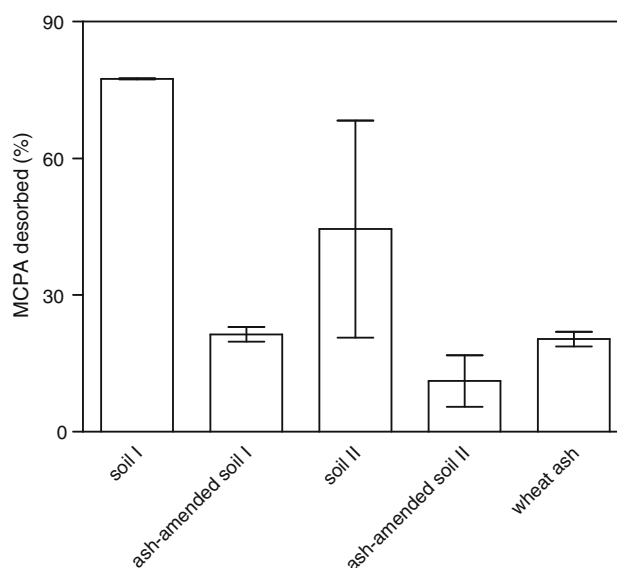[1] OC, organic carbon content; [2] Ill, illite; Chl, chlorite
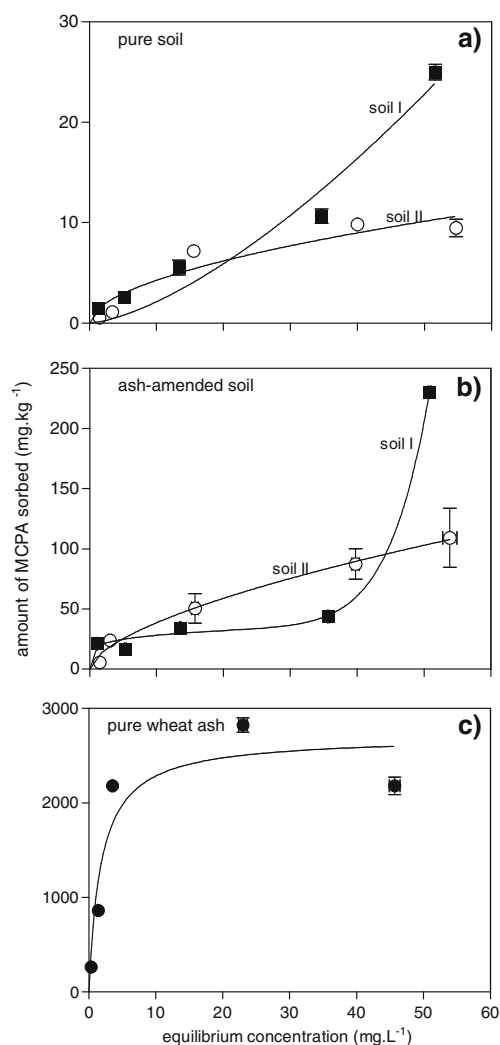
Fig. 1 Sorption of MCPA from water by pure soils, ash-amended soils and pure wheat ash. Error bars indicate the standard error of the mean

ash may resemble activated carbon as a surface adsorbent. Similar sorptive characteristics of wheat ash for neutral pesticides have been demonstrated and attributed to the fraction of elemental carbon in the ash (Yang and Sheng, 2003; Zhang et al., 2004). Wheat ash effectively sorbed MCPA, as shown in Figure. 1c. Wheat ash was 90-390 times and 230-1490 times more effective as a sorbent for MCPA than soil I and II, respectively. The efficacy of wheat ash in sorbing MCPA relative to the soils was dependent on the initial MCPA concentration used. At the equilibrium MCPA concentration of 1.50 mg.L^{-1}, the sorption coefficient was 615 L.kg^{-1}, demonstrating the much higher sorption of MCPA by wheat ash than by the two soils.

Compared to ash-free soils, sorption of MCPA by ash-amended soils was increased (Fig. 1b). The ash-amended soils I and II were approximately 8 and 16 times more effective than the ash-free soils I and II in sorbing MCPA, respectively. Assuming that the presence of wheat ash in soils did not change their sorption characteristics for MCPA, simple calculations show that 1% wheat ash contributed 85% and 91% to the sorption by ash-amended soils I and II, respectively. The soils, which formed 99% of the sorbent mass, sorbed only 9-15% of MCPA. At the equilibrium MCPA concentration of 1.50 mg.L^{-1}, the sorption coefficients were 16.0 L.kg^{-1} and 3.75 L.kg^{-1} for ash-amended soils I and II, respectively. As reported in earlier studies (Yang and Sheng, 2003; Zhang et al., 2004), the sorption capacity of the ash was reduced in the presence of soils. The reduced ash sorptivity for MCPA resulted presumably from the competitive sorption between the sorbate and various soluble soil organic molecules that occupied a portion of the ash surface. Despite competitive adsorption, the presence of 1% wheat ash in the soils significantly increased MCPA sorption.

Desorption of MCPA from the soils, ash-amended soils and pure wheat ash was expressed as a percentage of the total sorbed MCPA that was removed within the 24 hr of the desorption test (Fig. 2). The results clearly show that the presence of wheat ash in soils may also influence MCPA desorption. Up to 77% MCPA was desorbed from soil I, while only about 21% of the total MCPA sorbed by ash-amended soil I was removed. Similar influence of wheat ash on the MCPA desorption was observed for ash-amended soil II, when the addition of wheat ash to soil II increased the resistant fraction to desorption up to 80% (Fig. 2). The same resistant fraction to desorption was also observed for wheat ash alone, with only 20% of the MCPA

Fig. 2 Desorption of MCPA from soils, ash-amended soils and wheat ash. Error bars indicate the standard error of the mean

desorbed. No difference in the MCPA desorption between ash-amended soils and pure wheat ash indicates the predominance of wheat ash over soil in sorption-desorption behavior of the herbicide.

In summary, ash arising from the burning of wheat residue is a highly effective sorbent for the disociable herbicide MCPA. It increased the sorption of MCPA when present in the soils. The amendment of Fluvi-Gleyic Phaeozem and Eutric Regosol with 1% wheat ash (by weight) caused an 8-fold and 16-fold increase in MCPA sorption, respectively. Desorption of MCPA was also influenced by the presence of wheat ash in soils. The desorption results showed that 23-55% of sorbed MCPA were resistant to desorption in both soils. However, the addition of wheat ash to both soils increased the resistant fraction to 80%, which was the same as that in wheat ash alone. The field burning of crop residues appears to increase the sorption of pesticides in agricultural soils and decrease their leaching. As the burning of crop residues is still a common practice in Slovakia, applied herbicides in agricultural soils may be significantly immobilized due to the presence of ashes, and hence it may reduce the potential for it to leach into groundwater.

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