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Mucilage from seeds of chia (*Salvia hispanica* L.) used as soil conditioner; effects on the sorption-desorption of four herbicides in three different soils

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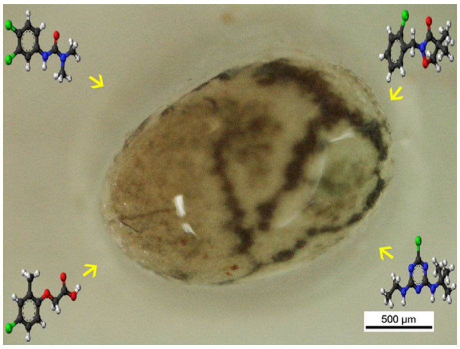
HIGHLIGHTS

- The effects of amendments with Chia seeds mucilage on physical properties of different agricultural soils were evaluated,
- Sorption-desorption processes of four herbicides was studied to assess the capability of amended soils to reduce their mobility,
- With amendments an improvement of soil microstructure was observed mostly in loam and in sandy-loam soils
- Sorption was more effective in the case of sandy loam- soil amended. Desorption was observed only for Terbuthylazine

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this work was to determine the effect of the mucilage extracted from Chia seeds (*Salvia hispanica* L.) as soil amendment on soil physical properties and on the sorption-desorption behaviour of four herbicides (MCPA, Diuron, Clomazone and Terbuthylazine) used in cereal crops. Three soils of different texture (sandy-loam, loam and clay-loam) were selected, and mercury intrusion porosimetry and surface area analysis were used to examine changes in the microstructural characteristics caused by the reactions that occur between the mucilage and soil particles. Laboratory studies were conducted to characterise the selected herbicides with regard their sorption on tested soils added or not with the mucilage.

Mucilage amendment resulted in a reduction in soil porosity, basically due to a reduction in larger pores (radius > 10 µm) and an important increase in finer pores (radius < 10 µm) and in partcles' surface. A higher herbicide sorption in the amended soils was ascertained when compared to unamended soils. The sorption percentage of herbicides in soils treated with mucilage increased in the order; sandy-loam < loam < clay-loam.

The increase in the organic carbon content upon amendment and the natural clay content of the soils are revealed to be responsible for the higher adsorption of Diuron when compared with Terbuthylazine, Clomazone and MCPA. Desorption of the herbicides was highly inhibited in the soils treated with mucilage; only Terbuthylazine showed a slight desorption in the case of loam and clay loam-soils.

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This study leads to the conclusion that mucilage from Chia seeds used as soil conditioner can reduce the mobility of herbicides tested in agricultural soils with different physico-chemical properties.

1. Introduction

Modern agriculture relies heavily on herbicides for the control of weeds in crops and pastures. These compounds can become serious pollutants because of their possible toxicity, long environmental persistence, and bioaccumulation factors, which can be a threat to human health. For this reason, the environmental fate of herbicides has been taken into account by many researchers.

Pimentel and Levitan (1986) described that $<0.1\%$ of the pesticide applied to crops actually reaches the target organism, while Celis et al. (2002) specified that most formulations of herbicides commonly used contains the active substance in immediately available form, which moves quickly toward points away from the site of application. Retention and mobility of herbicides in soil are related to the adsorption and desorption processes (Laor et al., 1996; Boesten, 1993; Martins and Mermoud, 1998), witch extension depends on soil properties (mostly organic matter and clay content) and on chemical characteristics of the herbicides used (Singh, 2002).

The sorption of pesticides in a soil–water system is governed by a mechanism whereby pesticide molecules partition into the soil colloidal phases (Celis et al., 1998; Chiou et al., 1979; Karickhoff et al., 1979). Many researchers (Cox et al., 2000; Hwang and Cutright, 2004; Ling et al., 2006; Nemeth-Konda et al., 2002, Barriuso et al., 1992; Murphy et al., 1992; Welhouse and Bleam, 1992; Baskaran et al., 1996, Cabrera et al., 2007, 2008, Guo et al., 1991) showed that the sorption of pesticides increases with increasing organic matter content, reducing the level of pesticide leaching in soil and, consequently, limiting their availability in the environment. Researches tried to reduce the mobility of pesticides using different organic amendments like animal manure, biosolids, municipal solid waste composts, crop residues, blood and bone meal, sea weeds and humic substances. Unfortunately, some of the amendmends used as soil conditioners have been shown to be sources of further contamination due to their heavy metal and organic toxic substances content, and high microbial load (Abad et al., 2005; Harrison et al., 2006; Selma et al., 2007).

Recently, plant exudates and Chia (*Salvia hispanica* L.) seed exudates, commonly used as analogue of root exudates, have been studied as possible soil conditioners (Beck et al., 1993; Naveed et al., 2017, Capitani et al., 2013, Luo et al., 2006).

Chia is an annual herbaceous plant of the Lamiceae family, which has been studied by many authors for its nutraceutical properties (Ayerza and Coates, 2005; Ixtaina et al., 2008; Vázquez-Ovando et al., 2009; Segura-Campos et al., 2014) and pharmaceutical application (Bochicchio et al., 2015).

Chia seed mucilage is mainly composed of xylose, glucose and glucuronic acid forming a branched polysaccharide (Lin et al., 1994; Muñoz et al., 2012), which structure has been confirmed by De la Paz Salgado-Cruz et al. (2013) using scanning image analysis.

The mucilage forms a gel when it is hydrated and it turns to hydrophobic after drying (Ahmed et al., 2014). Considering its rheological properties the Chia mucilage has been used as an experimental model for the study of plant-soil-water relations by Kroener et al. (2014). Ahmed et al. (2014) demonstrated that mucilage from the seeds of Chia facilitates water flowing into the root zone, increasing the soil hydraulic conductivity. To the best of our knowledge the effect of Chia mucilage on the soil porosity and relationship between mucilage and herbicide mobility have not been studied yet.

This study is aimed at testing the effect of amendment with Chia seed exudates on the sorption–desorption processes in three soils characterized by different physical-chemical properties.

The main parameters affecting the sorption process, such as the soil microstructure and pore space, were examined.

The mobility of four herbicides commonly used in cereal cultivations were evaluated too.

2. Materials and methods

2.1. Agricultural soils

The soil samples used for the laboratory studies were collected from the surface layer (0 to 30 cm) of three soils in the province of Potenza (Southern Italy), in the agricultural areas of Valle di Vitalba, Piani del Mattino and Costa della Gaveta.

Soils were air-dried and gently sieved to obtain aggregates up to 2 mm. The physical and chemical properties of the soils are reported in Table 1. An aliquot of 20 g of soil samples was used to determine the water saturation capacity (field capacity) that ranged from 42% (sandy loam soil) to 55% (loam and clay-loam soils).

2.2. Mucilage

Black chia seeds obtained from Eichenhain (www.eichenhain.com) were used to extract mucilage following the procedure described by Muñoz et al. (2012), briefly: 10 g chia seeds were mixed with 200 g distilled water (ratio 1:20 w:w) at 40 °C for 4 h in special containers lined with baking paper, dried in a stove at 50 °C for about 48 h and sieved at 1 mm, in order to eliminate any impurities. The residual water content of mucilage (10%) was determined gravimetrically after oven drying at 70 °C. The total C content (44.8% of dry matter) was determined by using an elemental analyzer (Primac SCN100, Skalar, The Netherlands) furnished with an infrared detector. The ash content of mucilage (4.5% of dry matter was determined by igniting the oven-dried sample in a muffle furnace at 440 °C.

2.3. Herbicides

Chemical structures of herbicides MCPA [(4-chloro-2-methylphenoxy)acetic acid], diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], clomazone [2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one] and terbuthylazine [2-N-tert-butyl-6-chloro-4-N-ethyl-1,3,5-triazine-2,4-diamine] are shown in Fig. 1. Herbicides used in experiments of adsorption-desorption were high purity products purchased from Sigma-Aldrich (St. Louis, MO, USA).

Physico-chemical characteristics of herbicides are shown in Table 2 (data from Trigo et al., 2010; DuPont, 2009; and Tomlin, 2006).

2.4. Mercury porosimetry

Samples of 1 g dry soils (sandy-loam, loam and clay-loam) were mixed with the mucilage at 2% w/w. Distilled water was added to bring soil samples to 30% of field capacity (Traoré et al., 2000) and left stand for 72 h. Control soil samples (without mucilage) were treated in the same way.

The distribution of pore radii of soil samples from 4×10^4 to 3.7 nm was determined using a mercury depression and intrusion porosimeter Autopore 9500 produced by Micromeritics, and instructions given by manufacturer. Small pieces of undisturbed soil aggregates were heated at 90 °C during 24 h and then outgassed at room temperature for 30 min before each experiment. A value for the surface tension of

Table 1
Physical and chemical parameters of tested soils measured according to the USDA methods.

Texture (Site)	pH_{H2O}	Sand	Silt	Clay	E.C. $_{1:2,5}$	C_aCO_3	Organic C Walkley-Black	N Kjeldahl
		(%)			(μS cm^{-1})	(g Kg^{-1})		
Sandy-Loam (Piani del Mattino)	7.93	76.5	16.8	6.7	210	17.86	5.46	0.5
Loam (Valle di Vitalba)	6.77	43.6	34.2	22.1	1149	8.19	17.74	1.9
Clay-Loam (Costa della Gaveta)	8.14	42.1	26.8	31.1	588	62.51	13.84	1.4

mercury of 0.48 N m^{-1} and a contact angle on soils of 141.3° were used with the Laplace equation assuming cylindrical pores in the calculations.

2.5. N_2-BET surface area analysis

Mucilage from Chia seeds was mixed with samples of 1 g dry soils in the proportion of 2% *w*/w and then hydrated with distilled water to 30% of field capacity and let dehydrate at room temperature. Control soil samples (without mucilage) were treated in the same way.

In this study, the surface area method by Brunauer et al. (1938) was used to determine the changes that occurred on the surface area and in the micropores of the stabilized specimens. The surface area was determined by assessing the physical adsorption of nitrogen gas by means of a micromeritics surface area analyzer ASAP 2420 produced by Micromeritics. This device is microprocessor-controlled and interacts with a personal computer, which allows a physisorption investigation. To run each test, approximately 0.15 g of the cured and dried sample was deposited into the sample holder, the sample was degassed for 1 h at 130 °C, nitrogen gas was then pumped into the sample, and the outer area value was estimated using the single-point BET (Brunauer, Emmett, and Teller) technique (Quantachrome Corporation, 2007).

2.6. Sorption and desorption studies

Adsorption of herbicides (MCPA, diuron, clomazone and terbuthylazine) on amended and non-amended soils was measured using a batch equilibration method according to OECD guideline 106 (OECD, 2000). Duplicate samples (0.5 g) of unamended and 10% (*w*/w) amended soil with mucilage were mixed dry thoroughly. Subsequently, 8 ml of herbicide solution at 1 mg l^{-1} concentration were added. Suspensions were shaken mechanically at 20 ± 2 °C for 24 h and then centrifuged at 5000 rpm for 10 min. An aliquot was filtered (0.45 μm, GHP filter) prior to analysis by high performance liquid chromatography (HPLC), using a chromatograph Waters 600E coupled to an UV detector (Waters 996). The determination conditions were: Nova-Pack C18 column (150 mm length × 3.9 mm i.d.) (Waters), mobile phase acetonitrile:water (40:60) for diuron and (50:50) for terbuthylazine. For MCPA the mobile phase consists of metanol:phosphoric acid pH 2 (60:40), and for clomazone the mobile phase was metanol:water (65:35). We used a mobile phase flow of 1 ml min^{-1}, a volume injection of 25 μl and detection to 250 nm for diuron, 220 nm for terbuthylazine, and 230 nm for MCPA and clomazone. For the quantitative analysis of herbicides external calibration curves were used with standard solutions of herbicides ranging between 0.1 and 2 mg l^{-1}. The percentage of pesticide adsorbed on the unamended or amended soil was calculated as: $\% Ads = [(Ci - Ce) / Ci] \times 100$. Sorption coefficient Kd (l kg^{-1}) was calculated with the equation $Kd = Cs / Ce$, Cs being the amount of herbicide sorbed on the unamended or amended soil $(Ci - Ce) \times V / M$, Ci being the pesticide initial concentration, Ce the equilibrium concentration, V the volume of pesticide solution added and M the soil mass.

Desorption of herbicides was measured immediately after adsorption by successive dilutions: 4 ml of supernatant were removed time by time for the desorption analysis and replaced with 4 ml of distilled water, samples were redispersed, shaken for another 24-h, centrifuged and the new concentration was determined up to the equilibrium was reached. This desorption cycle was conducted three times. Percentage of the herbicide desorption on the unamended or amended soil was determined as: $\% D = [(Cs - Csd) / Cs] \times 100$. Csd_n (mg Kg^{-1}) being the amount of pesticide desorbed from the unamended or amended soil $Cs_{n-1} - Cd_n$; Cd_n (mg Kg^{-1}) being the concentration of desorption $[Ce_n - (Ce_{n-1}/2)] \times V/M$.

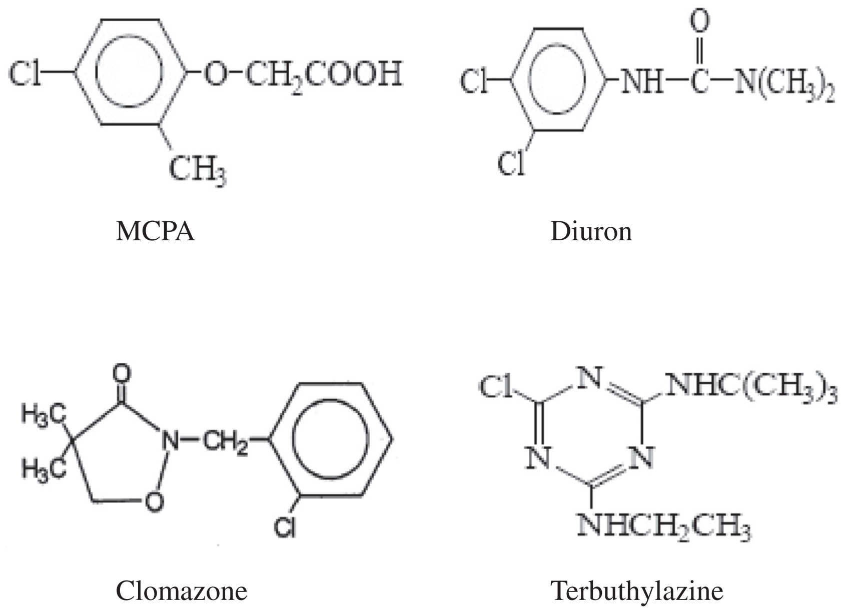
MCPA
Diuron
Clomazone
Terbuthylazine

Fig. 1. Chemical structures of herbicides.

Table 2
Physico-chemical characteristics of the herbicides used.

Herbicides	Molecular weight ($g\ mol^{-1}$)	Solubility in water (pH 7) ($mg\ l^{-1}$)	K_{ow} (log P) (pH 7)	pK_a
MCPA	200.6	293.9 mg/l (25 °C)	−0.71 (25 °C)	3.73 (25 °C)
Diuron	233.1	37.4 mg/l (25 °C)	2.85 ± 0.03 (25 °C)	13.2
Clomazone	239.7	1.1 g/l	2.5	–
Terbuthylazine	229.7	8.5 mg/l (20 °C)	3.21	2.0

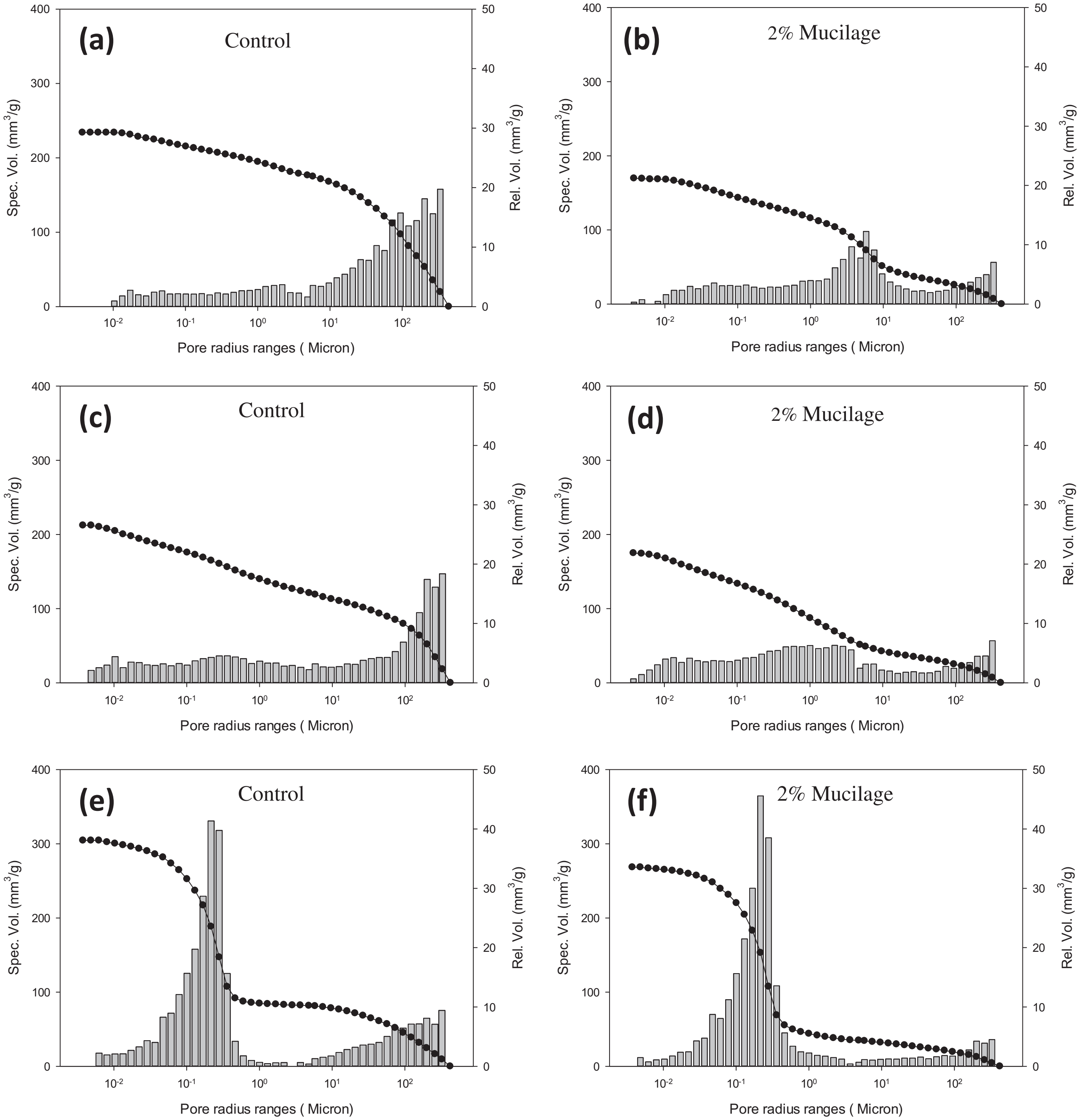

Fig. 2. Differential and cumulative mercury pore volume for the three soil samples sandy-loam (a – Control; b – 2% Mucilage), loam (c – Control; d – 2% Mucilage), and clay-loam (e – Control; f – 2% Mucilage), as a function of the calculated pore radius.

Table 3
Pore volumes ($mm^3\ g^{-1}$) of original unamended soil (Control) and amended soils (2% Mucilage), and cumulative volumes.

Range	Sandy-loam		Loam		Clay-loam	
	Control	2% Mucilage	Control	2% Mucilage	Control	2% Mucilage
0.00–0.01 μm	0.00	1.50	7.61	7.27	4.15	3.31
0.01–0.10 μm	18.66	24.68	29.13	34.10	47.85	44.87
0.10–1.00 μm	20.62	27.54	35.79	46.18	167.84	176.27
1.00–10 μm	30.73	69.61	29.40	46.90	8.00	12.97
10–100 μm	82.45	22.94	37.57	17.73	37.81	13.24
>100 μm	81.49	23.18	72.79	22.62	38.87	17.70
Cumulative volume	233.97	169.48	212.31	174.83	304.55	268.38

3. Results and discussion

3.1. Mercury porosimetry

Cumulative and differential mercury porosimetry curves of control and mucilage amended soils are shown in Fig. 2, and pore volumes ($mm^3\ g^{-1}$) in the different ranges in Table 3. In general the incorporation of mucilage in all tested soils has led to a reduction in total pore volume. Obviously, the effect was stronger in the sandy-loam soil and not so evident in the clay-loam soil. Data in Table 4 show that amended soils with mucilage undergo a large reduction of pores in the higher range studied (>10 μm) while, there was also a large increase of pores in the 0.1–10 μm range in the three soils under examination. As reported by Tisdall and Oades (1982) for other kind of organic amendment, the reduction of soil porosity caused by mucilage amendment can be due to the aggregation effect exerted by the organic material onto the soil particles with the consequent reduction of the free volume.

The pore size distribution curve shown in Fig. 2a is typical of a sandy soil characterized by the presence of large pores. The mucilage effect is mostly pronounced in this soil (Fig. 2b) due to the formation of small and medium pores and consequent reduction of largest soil pores.

In the loam soil the pore volume is equally distributed among particles of different radius in the range up to 10^2 μm and increase largely for particles of higher radius $>10^2$ μm (Fig. 2c). The amendment of mucilage provokes a dramatic reduction of free volume of particles in the range >10 μm (Fig. 2d). In the case of the clay-loam soil, the amendment of Chia mucilage causes a slight effect on largest particles leaving the distribution of the free volume almost unaltered (Fig. 2e, f).

3.2. N_2-BET surface area analysis

The specific surface area is an important characteristic to be examined for assessing changes in the soil structure, because most of the chemical reactions in soil takes place at the surface of particles (Mitchell and Soga, 2005). Fig. 3 shows the N_2-BET results for agricultural soils untreated and treated with the mucilage ($m^2\ g^{-1}$). A reduction in the surface area of the examined samples is important (nearly 50% reduction) in the clay-loam soil, which interacts better with the mucilage. The flocculation and growth of cementitious compounds among soil particles and into the pores yield a reduction in pore volume, which corresponds to a smaller surface area (Latifi et al., 2016; Eisazadeh and Eisazadeh, 2015).

3.3. Sorption experiments

3.3.1. MCPA

MCPA adsorption percentages in unamended soils and soils amended with mucilage are shown in Table 4. MCPA sorption significantly increased in the clay-loam soil added of mucilage in comparison to control. In loam and sandy-loam soils this effect was not so evident.

MCPA is an acidic herbicide, which is mainly present in the anionic form at soil pH > 6. Repulsion between MCPA anions and negatively charged surfaces in the clay-loam soil could be responsible of the low sorption percentage (10.45%). The addition of the mucilage is able to provide an organic surface on the clay particles largely present in this kind of soil causing an increased affinity (24.19%) for MCPA (Nearpass, 1976; Cabrera et al., 2008).

3.3.2. Diuron

Adsorption percentages - A(%) - and distribution coefficients - Kd ($l\ Kg^{-1}$) for diuron in the unamended soils and soils amended with mucilage, are given in Table 4. Diuron has a low solubility in water ($37.4\ mg\ l^{-1}$) and recorded the highest value in adsorption percentage and Kd when compared with the other herbicides, specially in the clay-loam soil, despite its lower OC content with respect to loam soil. The higher amount of clay content can also contribute to sorption of diuron in soils, as demonstrated for other substituted ureas (Barriuso et al., 1992; Murphy et al., 1992; Welhouse and Bleam, 1992; Baskaran et al., 1996). Increased adsorption of diuron was found in mucilage amended soils, with a very high augment in the case of the sandy-loam soil from 0.2 to 25% (Table 4). According to Gonzalez-Pradas et al. (1998) and Cox et al. (2007) the amount of organic matter in soil can affect sorption of diuron. These findings are in agreement with the chemical nature of the herbicide and with N_2-BET surface area values, which confirms a better interaction of mucilage with clay-loam soil.

In recent years, researchers are paying attention to the ability of clay minerals (natural or modified) to increase contaminant adsorption in soil (Cox et al., 1997; Rada Durović et al., 2009) and reduce pollution in water (Qurie et al., 2013; Khalaf et al., 2013). Clay minerals can be organically modified improving their surface affinity versus both ionic and neutral herbicides (Lagaly, 2001; Celis et al., 2002; Hermosín et al., 2006; Cornejo et al., 2008).

3.3.3. Clomazone

Clomazone sorption in the tested soils (unamended and amended) is lower than diuron and higher than MCPA. Clomazone is a highly polar and water soluble ($1.1\ g\ l^{-1}$) herbicide. Despite it exhibits a strong affinity for clay/humic associations (Cumming et al., 2002), Clomazone was sorbed at the same rate by clay-loam soil also when Chia mucilage was added. On the contrary, the adsorption on treated loam soil and

Table 4
Adsorption percentage – A (%) – and distribution coefficient – Kd ($l\ Kg^{-1}$) – of all herbicides tested in the unamended and amended soils.

Soils		Herbicides							
SS	T	MCPA		Diuron		Clomazone		Terbuthylazine	
		A(%)	Kd ($l\ kg^{-1}$)	A(%)	Kd ($l\ kg^{-1}$)	A(%)	Kd ($l\ kg^{-1}$)	A(%)	Kd ($l\ kg^{-1}$)
C-L	Control	10.45 ± 0.85	0.88 ± 0.15	46.11 ± 0.28	17.69 ± 0.20	27.10 ± 0.64	6.40 ± 0.20	36.78 ± 2.69	11.89 ± 1.30
	+ 10% T	24.19 ± 1.12	3.41 ± 0.25	53.32 ± 0.40	21.56 ± 0.36	27.44 ± 0.09	5.91 ± 0.03	47.75 ± 0.36	16.72 ± 0.24
L	Control	21.74 ± 0.03	3.17 ± 0.01	30.86 ± 1.09	9.51 ± 0.44	16.14 ± 0.25	3.42 ± 0.06	17.40 ± 0.62	4.81 ± 0.17
	+ 10% T	20.72 ± 0.31	2.67 ± 0.06	35.18 ± 6.82	10.70 ± 2.95	27.09 ± 0.45	5.81 ± 0.13	35.97 ± 1.77	10.42 ± 0.76
S-L	Control	20.59 ± 0.19	2.91 ± 0.04	0.20 ± 0.15	1.13 ± 0.03	1.02 ± 0.04	0.41 ± 0.01	0.22 ± 0.10	0.93 ± 0.018
	+ 10% T	20.75 ± 0.18	2.67 ± 0.04	24.95 ± 0.73	6.64 ± 0.23	10.46 ± 5.00	2.02 ± 0.94	35.62 ± 2.41	10.29 ± 1.02

Legend: SS = Selected Soils; T = Treatment with mucilage; C-L = Clay-Loam; L = Loam; S-L = Sandy-Loam; A(%) = percentage sorbed ± SD (three replicates).

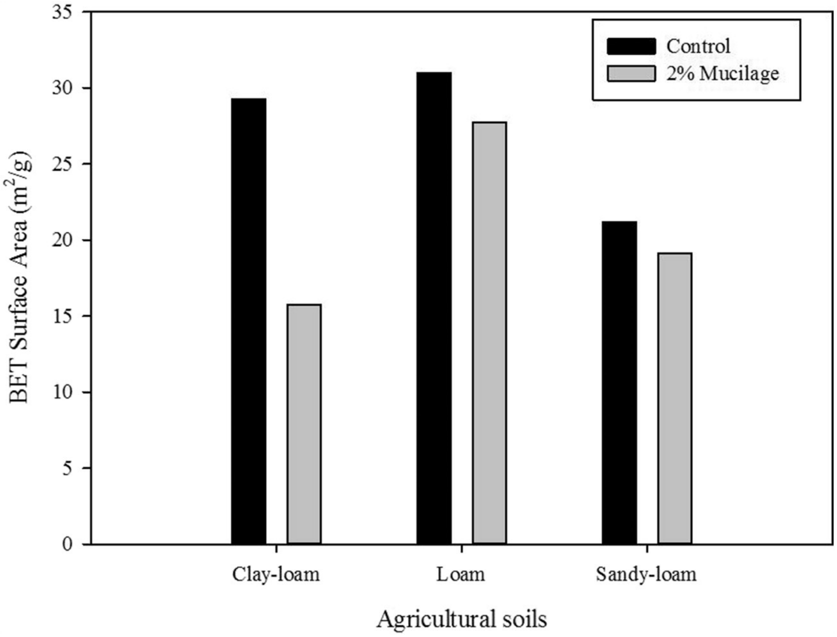

Fig. 3. N_2-BET results for untreated and mucilage-treated soils samples. Standard deviations on three replicates were ranging between 3 and 5% of the mean values (not reported).

sandy-loam soil increased considerably after the incorporation of mucilage (Table 4). The different behaviour observed in the clay-loam soil can be related to the great decrease in N_2-BET and total pore volume observed in this soil after treatment with the mucilage (Table 4 and Fig. 3).

3.3.4. Terbuthylazine

All soils tested in the adsorption experiment had high affinity for terbuthylazine, although not as high as diuron. After treatment with mucilage (Table 4), all soils showed an increased sorption of the herbicide, which was dramatically high in the case of sandy-loam soil. These results can be related to the low water solubility of terbuthylazine (8.5 mg l^{-1}) and the basic nature of this herbicide that determines a great affinity for the mucilage. As in the case of diuron, amended soils that gave a better response to treatment were loam and sandy-loam soils. These results are in agreement with a study conducted by Cabrera et al. (2007), who demonstrated an increasing sorption of diuron and terbuthylazine in soils added with an organic waste (alperujo).

3.4. Desorption experiment

3.4.1. Terbuthylazine

Percentages – D (%) – determined after every desorption cycle of terbuthylazine in the clay-loam and loam soils unamended and amended are shown in Fig. 4. The amounts released by the sandy-loam soil were imperceptible and are not shown. Lower desorption percentages were recorded in both soils treated with mucilage with respect to natural soils (from 71 to 53% and from 93 to 64%, in unamended and amended clay-loam and loam soils, respectively). This result is in

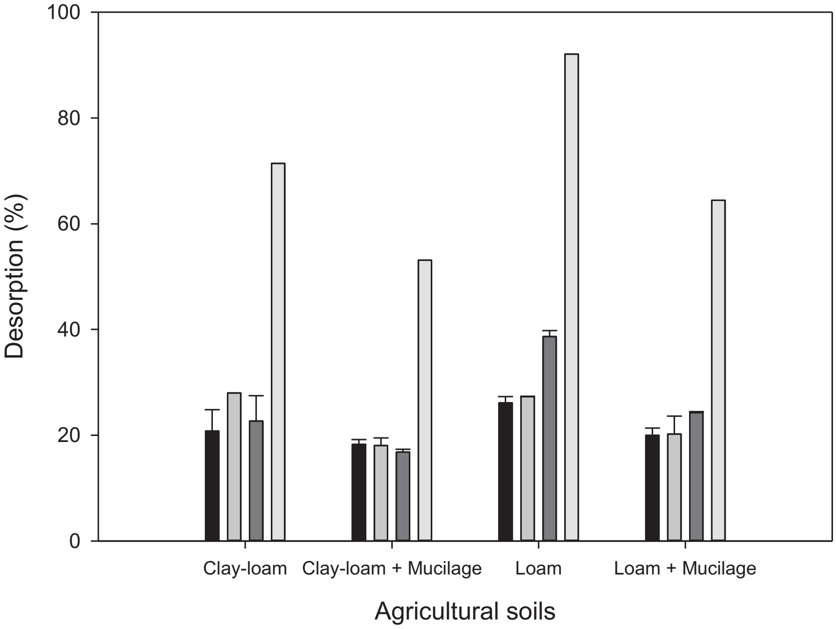

Fig. 4. Desorption percentage of terbuthylazine in unamended soils and amended with mucilage.

agreement with previous studies on soils treated with organic amendments (Cabrera et al., 2007). The release differences of MCPA, Diuron and Clomazone between treated and untreated soils were not detectable with the desorption method adopted.

4. Conclusion

Obtained results, according to statements reported in papers already published (Cox et al., 1997; Durović et al., 2009; Nemeth-Konda et al., 2002; Sing, 1998; Velázquez-Gutièrrez et al., 2015; White et al., 2003), indicate a good improvement of soil structure with organic amendment and an enhancement of herbicides' sorption reducing their mobility and consequently the possible contamination of the environment.

As reported in the introduction chapter, the application of organic materials as amendments of soils in field conditions could be responsible of further pollution if they maintain a high content of toxic elements (both metals and metalloids) and/or a large bacterial and fungal contamination.

Chia seed exudates and other kind of similar organic materials can avoid the addition of non-desired pollutants when used as soil amendment. In any case, the use of organic materials should be deeply evaluated before their application to soil in field conditions. The mass balance and the real efficiency of amendments as enhancers of the physical and chemical characteristics of the soil can vary considerably depending on the type and quality of the soil.

Conflict of interest

All funding sources for this study are listed in the Acknowledgment section of the paper. We do not have any patent pending, planned or issued relevant to the work. There are not other relationships, conditions or circumstances that present a potential conflict of interest.

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