Adsorption and Mobility of Linuron in Soils As Influenced by Soil Properties, Organic Amendments, and Surfactants

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Adsorption and mobility of the herbicide linuron (3−3,4-dichlorophenyl-1-methoxy-1-methylurea) in 35 irrigated soils with organic matter (OM) contents in the 0.43−2.59% range and in four natural soils with OM contents in the 4.16−11.69% range were studied using the batch equilibration technique. The adsorption isotherms were found to conform to the Freundlich adsorption equation. The Freundlich constant, K, and the distribution coefficient, K_d, were seen to be highly significantly correlated ($p < 0.001$) with the OM content when all soils or only those with an OM content above 2% were considered. There was also a significant correlation of K and K_d with the OM content ($p < 0.05$) and of K_d with the clay and silt plus clay contents ($p < 0.1$) when the soils with a OM content below 2% were considered. On the basis of the R_f values obtained by soil TLC, the pesticide was found to be slightly mobile in 77% and moderately mobile in 23% of the soils studied. The results of the leaching of linuron in soil columns unmodified and modified with two organic agricultural amendments, a city refuse compost, and two surfactants (one of them cationic and the other anionic) revealed that the leaching rate and the mass transfer of the herbicide to water were affected, increasing or decreasing according to the characteristics of the amendments and the doses added. These results also point to the usefulness of selected organic materials and surfactants in the development of physicochemical methods for preventing the pollution of soils, sediments and aquifers by hydrophobic pesticides.

Keywords: *Linuron; soil; adsorption; mobility; soil TLC; soil columns; organic amendments; surfactants*

INTRODUCTION

Organic contaminants, in general, and organic pesticides, in particular, are currently widespread in surface and groundwaters (Hallberg, 1989; Leistra and Boesten, 1989; Legrand et al., 1991; Sánchez-Camazano et al., 1995). This is creating an environmental problem that is increasingly attracting public awareness (principally in the United States and other developed countries). The frequent detection of pesticides in groundwaters means that the processes governing their behavior in the soil remain to be fully investigated and controlled.

Linuron (3−3,4-dichlorophenyl-1-methoxy-1-methylurea) is a urea derivative herbicide taken up mainly by the roots of plants. It was first introduced in 1960 and initially considered as the leading herbicide for potato cultivation in an international ranking (Roth, 1968). Since then, it has been used continuously in cultivations of carrots, onions, sunflower, several leaf vegetables, and bulbous ornamental plants. It is still widely used in the potato growing sector.

Some studies have been carried out on the adsorption and mobility of this herbicide in soils and on its applications and toxicology; these were compiled in a broad review published quite a few years ago by Maier-Bode and Hartel (1981). According to the works conducted on the adsorption of linuron in soils that were included in that review, which were generally carried out on small groups of soils (Hance, 1965; MacNamara and Toth, 1970), of all the urea herbicides linuron is

the compound that is adsorbed in the greatest amounts by the soil. The same review also included a work by Leh (1968), who concluded from experimental results that it would be difficult for the compound to access groundwaters. Later studies on adsorption−desorption (Valverde-García et al., 1989; Businelli et al., 1992), on factors that affect adsorption such as the herbicide-soil contact time and temperature (Brücher and Bergström, 1997; Cox and Walker, 1999) and on mobility (Smith and Emmond, 1975; Miliadis et al., 1987) of linuron have also reported the persistence and low mobility of this herbicide in the soil.

However, over the present decade the presence of linuron in aquifers has been detected with increasing frequency (Frank et al., 1990; Croll, 1991; Baci et al., 1994; Eke, 1994). Later, Caux et al. (1998) in research aimed at establishing the Canadian Water Quality Guidelines (CWQG) for linuron, detected up to 1100 and 2800 μg mL^{-1} of the herbicide in surface waters and groundwater, respectively, in zones subjected to intense cultivation. This, together with the widespread current use of the compound, make it essential to continue investigations into the different aspects involved in its adsorption and mobility in the soil.

Linuron is extensively used in irrigated areas of the province of Salamanca (Spain). Thus, in view of the above considerations, it was deemed interesting to study the adsorption and mobility of the herbicide in 35 soil samples with a broad range of OM contents from irrigated areas of the province. Also, considering the rather hydrophobic nature of linuron (log $K_{ow} = 3.00$) and the importance of organic matter, both solid and

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Table 1. Selected Characteristics of the Soils

soil	soil texture	soil type	pH	OM (%)	sand (%)	silt (%)	clay (%)	clay mineralogy[a]
irrigated soils								
1	loamy sand	Typic Xerofluvents	5.6	0.69	81.2	8.2	10.6	I,K,V
2	loamy sand	Typic Xerofluvents	5.0	0.80	84.3	6.0	10.7	I,K,V
3	sandy clay loam	Typic Rhodoxerafls	7.0	1.56	60.9	14.5	24.6	I,K,S
4	loamy sand	Typic Xerofluvents	7.0	1.51	73.4	12.7	13.9	I,K,V
5	loamy sand	Fluventic Eutrochrepts	6.0	1.44	75.1	11.3	13.6	I,K,S
6	loamy sand	Fluventic Eutrochrepts	5.9	0.94	78.4	10.0	11.6	I,K,V
7	loamy sand	Typic Xerofluvents	6.1	1.30	74.8	13.7	11.5	I,K
8	sandy loam	Typic Xerofluvents	7.2	1.22	60.6	19.2	20.2	I,K,V
9	loamy sand	Typic Xerofluvents	6.6	1.52	72.6	14.1	13.3	I,K,V
10	loamy sand	Fluventic Eutrochrepts	5.3	1.11	83.3	5.9	10.8	I,K,V
11	sandy loam	Calcic Rhodoxeralfs	7.5	0.77	66.4	15.5	18.1	I,K,S
12	loamy sand	Typic Xerofluvents	4.6	0.59	85.5	6.2	8.9	I,K,S
13	loamy sand	Fluventic Eutrochrepts	7.7	0.85	74.6	13.6	11.8	I,K
14	loamy sand	Typic Rhodoxeralfs	6.1	1.50	77.7	9.9	12.4	I,K
15	sandy clay loam	Calcic Rhodoxeralfs	7.2	0.78	66.3	12.8	20.9	I,K,S
16	sandy clay loam	Typic Xerofluvents	7.6	1.90	55.9	21.6	22.5	I,K,S
17	sandy clay loam	Typic Haploxeralfs	5.9	0.91	57.2	17.1	25.7	I,K,S
18	loamy sand	Typic Haploxeralfs	4.8	0.49	67.5	12.3	20.2	I,K,S
19	loamy sand	Typic Haploxeralfs	5.6	0.43	82.6	8.1	9.3	I,K,S
20	loamy sand	Typic Haploxeralfs	5.1	0.66	78.1	9.3	12.6	I,K,S
21	loamy sand	Psammentic Haploxeralfs	5.2	0.69	88.8	2.7	8.5	I,K,S
22	loamy sand	Typic Haploxeralfs	6.1	0.73	77.1	8.6	14.3	I,K,S
23	loamy sand	Psammentic Haploxeralfs	7.0	0.73	77.1	3.7	9.5	I,K,S
24	loamy sand	Calcixerollic Xerochrepts	7.0	0.87	82.7	5.8	11.5	I,K,S
25	loamy sand	Typic Xerofluvents	6.1	1.20	76.4	10.4	13.2	I,K,S
26	loamy sand	Typic Haploxeralfs	6.9	0.63	73.6	10.7	15.7	I,K,S
27	loamy sand	Typic Haploxeralds	4.4	0.67	84.7	8.1	7.2	I,K
28	loamy sand	Typic Xerofluvents	5.8	1.01	71.3	11.5	17.2	I,K
29	sandy loam	Typic Haploxeralfs	5.0	1.01	68.0	12.2	19.8	I,K,S
30	sandy loam	Aquic Haploxeralfs	6.1	1.00	69.1	12.9	18.0	I,K,S
31	loamy sand	Typic Haploxeralfs	5.0	0.97	72.8	6.7	20.5	I,K,S
32	loam	Typic Xerofluvents	5.4	2.59	35.8	45.7	18.5	I,K,C
33	loamy sand	Typic Xerofluvents	5.6	1.92	71.7	18.0	10.3	I,K,C
34	loamy sand	Psammentic Haploxeralfs	6.1	0.77	86.4	2.9	10.7	I,K,S
35	sandy clay loam	Calcixerollic Xerochrepts	7.3	2.04	56.6	10.8	32.6	I,K,C
natural soils								
36	clay loam	Calcic Haploxeralfs	7.6	4.16	22.2	42.9	34.8	I,K
37	loam	Lithic Ustochrepts	4.9	4.31	40.7	49.9	9.4	I,K,C
38	sandy loam	Dystic Ustochrepts	5.3	6.79	69.7	13.9	16.3	I,K,C
39	sandy loam	Lithic Ustochrepts	4.5	11.69	52.7	32.5	14.8	I,K,C

[a] I, illite; K, kaolinite; S, smectite; V, vermiculite; C, chlorite.

dissolved, in the adsorption and mobility of hydrophobic or nonionic pesticides (Caron et al., 1985; Chiou, 1989; Santos-Buelga et al., 1992; Celis et al., 1998), another aim of this work was to study the effect of a series of organic amendments or additives and surfactants, which in agricultural practices may coincide with the presence of the herbicide, on the mobility of linuron in soil columns. This second objective is in turn a further contribution to the knowledge of the potential use of organic materials and surfactants to solve problems related to the pollution of soils and aquifers by hydrophobic pesticides.

MATERIALS AND METHODS

Chemicals. Unlabeled linuron (>99% technical purity), linuron metabolites, and ^{14}C-labeled linuron with a specific activity of 1.31 MBq mg^{-1} (99% purity) were supplied by AgrEvo (Frankfurt, Germany). Linuron is a liquid hydrophobic pesticide with a water solubility of 81 mg L^{-1} at 25 °C and a K_{ow} of 1010 (Tomlin, 1995). The toxicity class of this herbicide according to EPA is III (Tomlin, 1995).

Soils. Table 1 lists the types of soils used (Soil Survey Staff, 1994) and some selected characteristics. Samples of top soils (0–15 cm) were collected. Soils 1–35 were from different irrigated areas of the province of Salamanca, while soils 36–39 were natural uncultivated soils. The latter, with organic matter (OM) contents above 4%, were included owing to the low OM contents (0.43–2.59%) of the irrigated soils and the

high significance of this parameter with respect to hydrophobic pesticide adsorption and mobility in soils and with a view to expanding the scope of the study. Soil 34 was used for linuron leaching studies in soil columns. Samples were air-dried and sieved through 2 mm mesh. Their particle size distribution was determined using the pipet method (Day, 1965). Organic carbon was determined according to a modified version of the Walkley–Black procedure (Jackson, 1958), the results being multiplied by 1.72 for conversion into OM contents. Soil pH values were measured in slurries made up at a 1:1 soil/water ratio. Clay minerals were qualitatively identified by the X-ray diffraction technique (Robert, 1975).

Amendments. The organic amendments employed were the following: a city refuse compost (CRC) from the urban solid waste treatment plant at Valdemingomez (Madrid, Spain), the characteristics of this CRC have been described by Diaz-Marcote (1995); two commercial organic amendments used in agricultural practices, one was a peat called Torficosa (P) (Plantaflor humus, Veraufs GmbH, Vechia, Germany) and the other was a liquid humic amendment called Humimag (LHA) (Braker laboratories, S. L. Valencia, Spain)—their characteristics have been described by Liñan (1998). The surfactants employed were sodium dodecyl sulfate (SDS), an anionic surfactant, and tetradecyltrimethylammonium bromide (TDTMA), a cationic surfactant. Both were supplied by Aldrich Chemical Co. (Milwaukee, WI). The critical micellar concentration (CMC) for SDS is 2.38 g L^{-1} and for TDTMA it is 0.10 g L^{-1}.

The total organic carbon contents of the amendments determinated as described above for the soils were as follows:

28.1% for CRC; 53.3% for P; 22.1% for LHA; 22.1% for SDS; and 62.7% for TDTMA.

Adsorption. Adsorption experiments were carried out using the batch equilibration technique. Soil samples of 2 g were equilibrated with 10 mL of an aqueous solution of linuron at concentrations of 15, 20, 25, 30, 35, and 40 μg mL^{-1}. Soil suspensions were shaken mechanically at 20 ± 2 °C in 15 mL glass centrifuge tubes closed with Teflon lined caps for 24 h. Preliminary experiments revealed contact for 24 h to be long enough for equilibrium to be reached. Subsequently, the suspensions were centrifuged at 5045g for 30 min. The linuron concentration in the supernatant was determined by HPLC using the method previously set up by the authors of this work for the determination of linuron in aqueous soil extracts (Sánchez-Martín et al., 1996). The apparatus used was a Waters chromatograph (Waters Assoc., Milford, MA) equipped with a model 600E multisolvent delivery system attached to a model 717 autosampler, a model 996 photodiode array detector, and a Millennium 2010 chromatography manager data acquisition and processing system. A Waters Nova Park C-18 column (159 × 3.9 mm, particle diameter 5 mm) was used at ambient temperature. The detection limit of linuron was 0.010 μg mL^{-1}. The amount of pesticide adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the soil. The experiments were conducted in duplicate with standards and blanks included in each series.

Soil Thin-Layer Chromatography (Soil TLC). Soil plates for TLC were prepared by grinding the soil samples in a mortar followed by sieving through 160 μm mesh. Soil (7.5 g) and distilled water (15 g) were slurried and spread as a 0.5 mm thick layer over 20 × 5 cm^2 glass plates with the aid of a Desaga TLC spreading device. The three central plates in each set of five prepared for each type of soil were chosen for subsequent experiments. The selected plates were dried at room temperature and subsequently stored in a desiccating chamber at a relative humidity of 70%. The plates were marked with two horizontal lines at distances of 2 and 12 cm, respectively, from the base. A 7 μL droplet of ^{14}C-linuron (342 Bq) was spotted on the baseline of the three plates with the aid of a micropipet. The plates were placed in closed individual glass chromatography chambers 22 cm long and 5 cm wide, using distilled water as the developer. After the distilled water had migrated to a distance of 10 cm from the baseline, the plates were allowed to dry at room temperature. The movements of ^{14}C-linuron were detected using a Berthold TLC Tracemaster 20 linear analyzer. The mobility factor, R_f, is given by $R_f = R_l/10$, where R_l is the frontal distance travelled by the herbicide.

Soil Column Leaching. Leaching columns were constructed from poly(vinyl chloride) (PVC) pipe and were 40 cm long and 5 cm i.d. They were prepared according to the method from Weber (1986). Each column was packed with 600 g of dry soil and water-saturated by placing them into a tank and increasing the water volume in the tank until it topped the columns. Then, each column was allowed to drain for 48 h so that it could attain humidity conditions equivalent to the field capacity, after which the different amendments were added. Two different doses of each amendment were used: 2 t ha^{-1} and 15 t ha^{-1} (as total carbon). These were applied and mixed with 50 g of soil taken from the upper part of the column, and 25 mL of water was added to the column. After 5 days, 5 mL of a solution of linuron at 1000 μg mL^{-1} in methanol was added to the top part of the unamended and amended columns. The columns were then washed with 1980 mL (101cm) of water, applying 60 mL to each of them for 33 days. Column leachates were monitored daily for herbicide contents. After being allowed to drain for some time, the columns were cut into segments breadthwise at 10 cm intervals. The soil contained in each segment was turned over and weighed. Then, five samples of 5 g each were taken from each segment. Two such samples were used to determine the moisture content of the soil from the weight loss measured upon treatment at 80 °C for 12 h. The other three samples were employed to determine linuron contents. Triplicate 5 g soil samples were shaken for
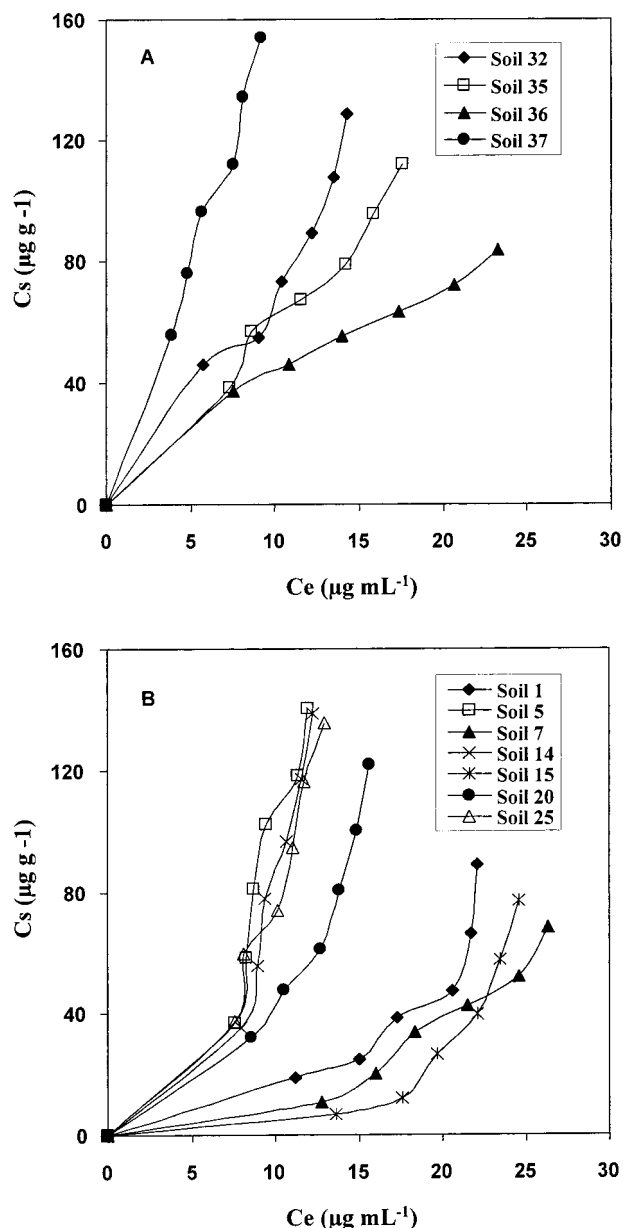

Figure 1. Selected adsorption isotherms of linuron by soils with OM contents above 2% (A) and below 2% (B).

24 h with 10 mL of methanol. The concentration of linuron in the methanolic solution was determined by HPLC as described previously (Sánchez-Martín et al., 1996). The extraction efficiency, measured previously with soil samples spiked with different amounts of linuron, was >92%. All column experiments were carried out in duplicate. Conservative tracer transport, using chloride (KCl) as an ion tracer, was implemented to describe the dispersive characteristics of each column used in the pesticide transport studies. The amount of chloride ion applied was 30 mg and the water flow rate was the same as that used in the pesticide leaching studies. The pore volume (PV = 200 mL) of the packed columns was determined by the weight difference of water-saturated columns versus dry columns.

RESULTS AND DISCUSSION

Adsorption Studies. The adsorption isotherms of linuron by the 39 soils were determined. Figure 1 shows selected isotherms of soils with OM contents above 2% and below 2%. All isotherms fit the Freundlich equation with a correlation coefficient of $r \geq 0.93$. The linear form

Table 2. Freundlich Constants (*K*, *n*), Distribution Coefficients (*K*$_d$), log *K*$_{om}$, and *R*$_f$ Values

soil	*K*	*n*	*K*$_d$[a]	log *K*$_{om}$	*R*$_f$
irrigated soils					
1	0.11 ± 0.03[b]	0.48 ± 0.01[b]	1.29 ± 0.33[b]	1.18	0.30 ± 0.00[b]
2	0.67 ± 0.06	0.58 ± 0.03	3.55 ± 0.34	1.92	0.39 ± 0.01
3	5.10 ± 0.99	1.08 ± 0.05	4.28 ± 0.83	2.51	0.22 ± 0.01
4	8.82 ± 0.86	1.43 ± 0.04	4.41 ± 0.43	2.77	0.25 ± 0.01
5	0.24 ± 0.44	0.39 ± 0.05	9.47 ± 1.56	1.22	0.26 ± 0.01
6	0.38 ± 0.03	0.52 ± 0.03	3.09 ± 0.24	1.60	0.28 ± 0.02
7	0.02 ± 0.01	0.41 ± 0.05	0.65 ± 0.39	0.27	0.29 ± 0.01
8	0.32 ± 0.05	0.55 ± 0.03	2.18 ± 0.37	1.42	0.24 ± 0.02
9	3.55 ± 0.50	0.84 ± 0.04	5.59 ± 0.77	2.37	0.19 ± 0.02
10	0.34 ± 0.06	0.44 ± 0.03	6.52 ± 1.06	1.49	0.27 ± 0.01
11	0.04 ± 0.03	0.45 ± 0.03	0.58 ± 0.47	0.67	0.21 ± 0.01
12	0.01 ± 0.01	0.37 ± 0.01	0.50 ± 0.14	0.23	0.45 ± 0.04
13	0.01 ± 0.01	0.36 ± 0.06	0.46 ± 0.42	0.07	0.49 ± 0.03
14	0.07 ± 0.03	0.33 ± 0.03	7.79 ± 3.03	0.67	0.23 ± 0.01
15	0.01 ± 0.01	0.34 ± 0.02	0.86 ± 0.74	0.11	0.30 ± 0.01
16	0.56 ± 0.07	0.52 ± 0.03	4.87 ± 0.59	1.44	0.21 ± 0.01
17	1.69 ± 0.10	0.56 ± 0.02	10.38 ± 0.69	2.27	0.40 ± 0.01
18	0.09 ± 0.01	0.51 ± 0.02	0.84 ± 0.13	1.27	0.31 ± 0.02
19	1.45 ± 0.07	0.66 ± 0.04	4.73 ± 0.23	2.53	0.36 ± 0.03
20	0.30 ± 0.08	0.47 ± 0.02	4.21 ± 1.14	1.66	0.33 ± 0.04
21	1.05 ± 0.01	0.73 ± 0.04	2.45 ± 0.04	2.18	0.35 ± 0.00
22	0.06 ± 0.03	0.35 ± 0.04	4.20 ± 2.03	0.94	0.41 ± 0.01
23	0.01 ± 0.01	0.36 ± 0.01	0.58 ± 0.42	0.14	0.27 ± 0.02
24	0.18 ± 0.07	0.47 ± 0.03	2.43 ± 0.95	1.33	0.40 ± 0.04
25	0.49 ± 0.06	0.46 ± 0.04	7.79 ± 0.84	1.61	0.26 ± 0.02
26	0.53 ± 0.04	0.49 ± 0.02	5.65 ± 0.47	1.93	0.33 ± 0.01
27	0.30 ± 0.02	0.59 ± 0.05	1.52 ± 0.14	1.65	0.33 ± 0.02
28	0.52 ± 0.03	0.55 ± 0.03	3.55 ± 0.19	1.71	0.23 ± 0.01
29	1.20 ± 0.08	0.48 ± 0.04	14.99 ± 1.03	2.07	0.35 ± 0.03
30	12.72 ± 2.15	0.89 ± 0.05	16.75 ± 2.86	3.10	0.26 ± 0.01
31	3.07 ± 0.38	0.76 ± 0.01	6.36 ± 0.79	2.50	0.29 ± 0.01
32	5.78 ± 0.40	0.90 ± 0.04	7.48 ± 0.51	2.35	0.18 ± 0.02
33	5.86 ± 0.30	0.92 ± 0.02	7.27 ± 1.14	2.48	0.19 ± 0.03
34	2.60 ± 0.31	1.21 ± 0.07	1.73 ± 0.11	2.53	0.40 ± 0.01
35	6.33 ± 0.24	1.20 ± 0.03	4.31 ± 0.03	2.49	0.25 ± 0.04
natural soils					
36	9.86 ± 0.22	1.16 ± 0.03	7.12 ± 0.41	2.37	0.17 ± 0.03
37	10.34 ± 0.45	1.29 ± 0.03	6.22 ± 0.05	2.38	0.17 ± 0.01
38	25.41 ± 0.26	1.21 ± 0.01	16.83 ± 0.63	2.57	0.11 ± 0.02
39	51.34 ± 1.19	1.09 ± 0.05	41.15 ± 6.23	2.64	0.11 ± 0.02

[a] $C_e = 10$ μg mL^{-1}. [b] Mean values ± standard deviation of two replicates.

of this equation is expressed as log C_s = log K + 1/n log C_e, where C_s is the amount of herbicide adsorbed (μg g^{-1}), C_e is the equilibrium concentration of herbicide in solution (μg mL^{-1}), and K and n are characteristic constants of the herbicide adsorption. K is the amount adsorbed for an equilibrium concentration of 1 μg mL^{-1} and, hence, represents adsorption at low concentrations, and n reflects the variation in adsorption with the concentration (curvature of the isotherms). Since in some cases the values of n departed from unity, the distribution coefficients, K_d, were also determined. The distribution coefficient is the relationship between the amount of herbicide in the soil and in the equilibrium solution for a given equilibrium concentration; in this case, it was calculated for $C_e = 10$ μg mL^{-1}. The values of n, K, and K_d obtained are shown in Table 2 and were used to compare the adsorption of linuron by the different soils. Table 2 also shows the values of K normalized at 100% OM (K_{om}= 100K/% OM).

The n values corresponding to the adsorption isotherms of the herbicide by soils are in general lower than unity and sometimes very low, indicating a strong increase in adsorption with the rise in concentration. The n values are characteristic of type S isotherms in the classification of Giles et al. (1960) and show a marked convex initial curvature, indicating the low affinity of the soils for linuron at low herbicide concentrations. Adsorption isotherms of linuron with low n

values have also been obtained by Valverde-García et al. (1989) and by Businelli et al. (1992). The n values corresponding to the isotherms of the soils with an OM content above 2% are close to unity. In some cases, these isotherms are of the S type, with a very small initial convex curvature, while in others they are of the L type, with little initial concave curvature. The L type isotherms are typical of high affinity of the adsorbent for the adsorbate. In both cases, they are very close to type C isotherms, which are linear and indicate that a constant partition of linuron between the water and the organic matter of the soil occurs.

Nonlinear sorption for other phenylureas (fenuron, monuron, diuron) has been reported by Spurlock (1995) and by Spurlock and Biggar (1994). In a thermodynamic study on the partition of organic compounds in soils Spurlock and Biggar (1994) concluded that the fundamental sorption process for these compounds, containing polar groups in their molecule, is more complex than hydrophobic theory suggests, and specific interactions must occur between these herbicides and the OM and also, when the OM content is low, with the mineral fraction.

The values of the K constant lie within the 0.01−51.34 range, the highest values corresponding to soils with high organic matter contents. The K_d values are much higher than those of K when the value of n is low and in some soils are up to 16 times higher than the value

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Table 3. Simple Correlation Coefficients (*r*) between Freundlich Constants (*K*), Distribution Coefficients (*K*$_d$), and Soil Characteristics

soils	constants	pH	OM	clay	silt + clay
all soils	K	−0.24	0.95[a]	0.12	0.38[b]
	K_d	−0.32[b]	0.82[a]	0.13	0.32[b]
OM < 2%	K	0.10	0.42[b]	0.20	0.26
	K_d	−0.18	0.35[b]	0.32[c]	0.31[c]
OM > 2%	K	−0.59	0.99[a]	−0.41	−0.42
	K_d	−0.59	0.97[a]	−0.39	−0.35

[a] Significant at <0.001 level. [b] Significant at 0.05−0.01 level. [c] Significant at <0.1 level

of *K*. When *n* departs only slightly from unity, the K_d values are close to those of *K*.

The influence of soil components on linuron adsorption was determined using a statistical approach. The single correlations between *K* or K_d and the different chemical and textural properties of the soils were determined by least-squares linear regression analysis (Table 3). First, all the soils were considered together. Then, two soil groups were considered: soils with an OM content above 2% and soils with an OM content below 2%.

When all the soils were considered, a highly significant correlation ($p < 0.001$) was found between both *K* and K_d and the OM content, and a significant correlation ($p < 0.05$) was obtained between both constants and the silt plus clay content. This indicates that the OM content is the most significant parameter in the adsorption of linuron by soils with widely varying OM, silt, and clay contents. On the basis of the determination coefficient, r^2, the OM content accounted for 90% of the variance in adsorption. The results were also subjected to multiple linear regression analysis by combining two or more variables, but the correlation coefficients (R^2) obtained provided no further explanation for the adsorption variability as compared with to the single correlation coefficients (r^2). R^2 was 0.90 for the multiple correlation between K and OM and silt + clay and 0.68 for the multiple correlation between K_d and pH, OM, and silt + clay.

When the soils with OM contents above 2% were considered, a highly significant correlation ($p < 0.001$) also was found between both *K* and K_d constants and the OM content. However, there was no correlation between the adsorption constant and the content in either clay or silt plus clay. The determination coefficient for the correlation between K and the OM content accounts for 98% of the variance in adsorption. Accordingly, linuron adsorption in soils with a high OM content must depend almost solely on the OM content.

The correlation coefficient between *K* and K_d constants and the OM content was significant ($p < 0.05$) but low when only the soils with an OM content below 2% were considered. An insignificant correlation ($p < 0.1$) was also observed between K_d and the clay and silt plus clay contents. These correlations point to little influence of the OM fraction in linuron adsorption and the influence of the silt plus clay fraction when the concentration of the herbicide in solution is increased. This influence was not observed when only the soils with OM > 2% were considered. These results are consistent with the adsorption isotherms corresponding to these soils which, as mentioned above, are of the S type according to the classification of Giles et al. (1960), with very low *n* values, and also with the broad range of variation of log K_{om} for these soils (0.07−3.10) (Table

Table 4. Simple Correlation Coefficients (*r*) between R_f and Soil Characteristics

soils	K	K_d	pH	OM	clay	silt + clay
all soils	−0.55[a]	−0.46[b]	−0.05	−0.64[a]	−0.29[d]	−0.56[a]
OM < 2	−0.32[d]	−0.20	−0.19	−0.64[a]	−0.21	−0.34[d]
OM > 2	−0.79[c]	−0.74[d]	0.71[d]	−0.84[c]	0.57	0.15

[a] Significant at <0.001 level. [b] Significant at 0.01−0.001 level. [c] Significant at 0.05−0.01 level. [d] Significant at <0.1 level.

2). The influence of the mineral fraction in the adsorption of the urea herbicide thiazafluron at high herbicide concentrations by soils with low OM contents has also been reported by Cox et al. (1995), and this influence is frequent in the adsorption of moderately hydrophobic pesticides with polar groups in their molecule (Calvet, 1989; Sánchez Martín et al., 1993).

According to the high correlation between K and the OM content for the soils with OM contents above 2%, the corresponding values of log K_{om} vary over a very narrow range (2.35−2.64), with a mean of 2.47. This mean value lies within the 2.46−2.54 range reported by Tomlin (1995) as reference values of this constant for the adsorption of linuron by soil organic matter and is higher than the theoretical value of log K_{om} (2.25) determined from the log K_{ow} of linuron using the equation proposed by Briggs (1981) for substituted phenylureas. However, in a study of linuron adsorption by six soils with OM contents in the 3.02−67.8% range, Hance (1965) found a mean log K_{om} value of 2.80, which is higher than that found in the present work.

Finally, regarding the results obtained on the influence of the contents in OM, silt and clay in the adsorption of linuron, it is noteworthy that not only the content in these colloidal fractions must play an important role in the adsorption of the herbicide but also that the nature of these fractions must be important. In this sense, Morita (1976) reported that the adsorption of linuron by the OM increases with its degree of humification, quantified by the rubbed fiber content and by the pyrophosphate index. Also, in a study on the adsorption of linuron by different clay minerals, Süss and Wagner (1970) highlighted the influence of the nature of these minerals.

Soil TLC Mobility Studies. The R_f values obtained from soil TLC (averages of three determinations) used to study linuron mobility are shown in Table 3. When all the soils are considered, the R_f varies between 0.11 and 0.49 (mean 0.28). For soils with an OM content above 2% it varies between 0.11 and 0.25 (mean 0.17) and for the soils with an OM content below 2% between 0.19 and 0.49 (mean 0.34). According to the classification of Helling and Turner (1968) linuron can be predicted to be slightly mobile in 77% and moderately mobile in 23% of the soils studied. R_f values for linuron mobility similar to those obtained in the present work have been reported by Pestemer (1977) (0.07−0.30) for four soils with OM contents between 1.03 and 34.08%.

Table 4 shows the simple correlation coefficients between R_f and K, K_d, and the properties of the soils. When all the soils are considered, a highly significant negative correlation ($p < 0.001$) can be seen between R_f and K, the OM content, and the silt plus clay content. These correlations, with a higher or lower degree of significance, were also observed in the group of soils with an OM content below 2%. In the soils with an OM content above 2%, the R_f was not significantly correlated with the content in silt plus clay. The correlation
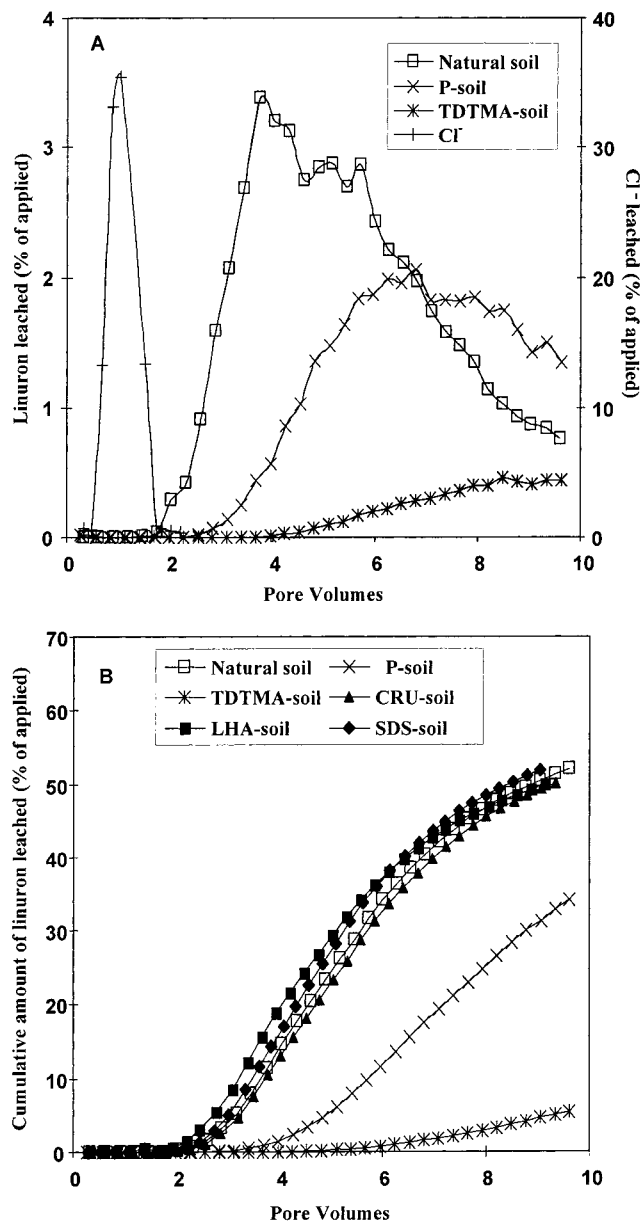
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Figure 2. Breakthrough (A) and cumulative (B) curves for linuron leaching in unamended soil and in soil amended with 2 t ha^{-1} of the different organic matters and surfactants.

coefficients between R_f values and soil properties are in general lower than the correlations found between K and K_d and these properties. Additionally, the correlation coefficients between R_f and K and K_d are relatively low. This is because the adsorption governing the mobility of the herbicide as measured by soil TLC does not occur under conditions of equilibrium while in the study of adsorption by the batch technique, by definition adsorption occurs under conditions of quasi-equilibrium. Because adsorption does not take place in the soil under conditions of equilibrium either, some authors consider the information obtained by soil TLC to be more relevant than that obtained by the traditional batch technique with respect to the behavior of pesticides in soils (Johnson and Sims, 1998).

Soil Columns Studies. Figure 2 shows the breakthrough and cumulative curves of the leaching of linuron in columns of unamended soil and soil amended with the low dose (2 t ha^{-1}) of P and TDTMA. The curves corresponding to the soils amended with the

Table 5. Amounts of Linuron Retained (% of Applied) in Soil Columns Amended with Organic Matters

amendments	segment (cm)			
	0−10	10−20	20−30	30−40
none	1.65	4.05	5.35	6.43
P(D1)[a]	7.13	6.99	7.07	7.80
P(D2)[b]	56.77	3.48	3.59	1.99
LHA(D1)	1.46	4.34	4.97	5.63
LHA(D2)	1.15	3.12	4.46	5.36
CRC(D1)	0.98	3.28	4.28	6.17
CRC(D2)	21.78	2.11	2.53	3.50
TDTMA(D1)	48.91	6.09	4.44	3.43
TDTMA(D2)	78.36	0.24	0.09	0
SDS(D1)	0.92	3.61	3.41	6.56
SDS(D2)	0.22	0.98	1.01	1.61

[a] D1, dose 2 t ha^{-1} (LSD at 95% between segments and treatments = 1.43). [b] D2, dose 15 t ha^{-1} (LSD at 95% between segments and treatments = 1.47).

same dose of the LHA, CRC, and SDS were similar to those of the unamended soil. Figure 2 also shows the leaching curve of the chloride tracer ion, which is almost identical for the amended and unamended columns.

Percolation of the chloride ion, which is a conservative ion and hence does not undergo retention or degradation in soils and which indicates the movement of water, begins at 0.5 PV and shows a peak at about 1 PV, as is generally expected to occur in the percolation of conservative ions (Biggar and Nielsen, 1962). In the percolation curves of linuron in unamended soils and in soils amended with LHA, CRC, and SDS, the start of leaching is shifted toward the 1.38−1.74 PV zone and the maximum of the curve toward the 3.11−3.75 PV zone. These shifts are much greater for the soils amended with P and with TDTMA, in which the start of leaching occurs at 2.56 and 3.67 PV, respectively, and maxima are seen at 6.79 PV (P) and even 8.48 PV (TDTMA). The amount of linuron leached represents approximately 50% of that applied to the columns for the natural soil or the soil amended with LHA, CRC, and SDS and decreases to 34.2% in the case of the column amended with P and it becomes as low as 5.48% for the column amended with TDTMA.

The residual linuron of the columns (Table 5) in unamended soil or in soil amended with LHA, CRC, and SDS accumulates in the deeper segments; in the soil amended with P it is distributed in a more homogeneous fashion and in the soil amended with TDTMA it is mainly accumulated in the first segment.

Figure 3 shows the breakthrough and cumulative curves of the leaching of linuron in soil columns amended with the high dose (15 t ha^{-1}) of the different additives. The percolation curve corresponding to the soil modified with LHA is fairly similar to that of natural soil (Figure 2A). Some differences, however, may be seen: thus, leaching begins at a lower PV (0.8 PV) and displays an inflection at approximately 3 PV. Both effects must be due to the rapid initial leaching of the linuron adsorbed by the dissolved OM of this amendment. The rapid initial leaching is also seen in the corresponding cumulative curve. The maximum of the breakthrough curve in the column amended with CRC is delayed up to 6.22 PV and the maximum in the percolation curve of the columns amended with P and with TDTMA is not achieved with the flow of water added. Accordingly, the maximum occurs at a PV value above 9.5. The breakthrough curve of linuron in the column amended with SDS differs strikingly from the
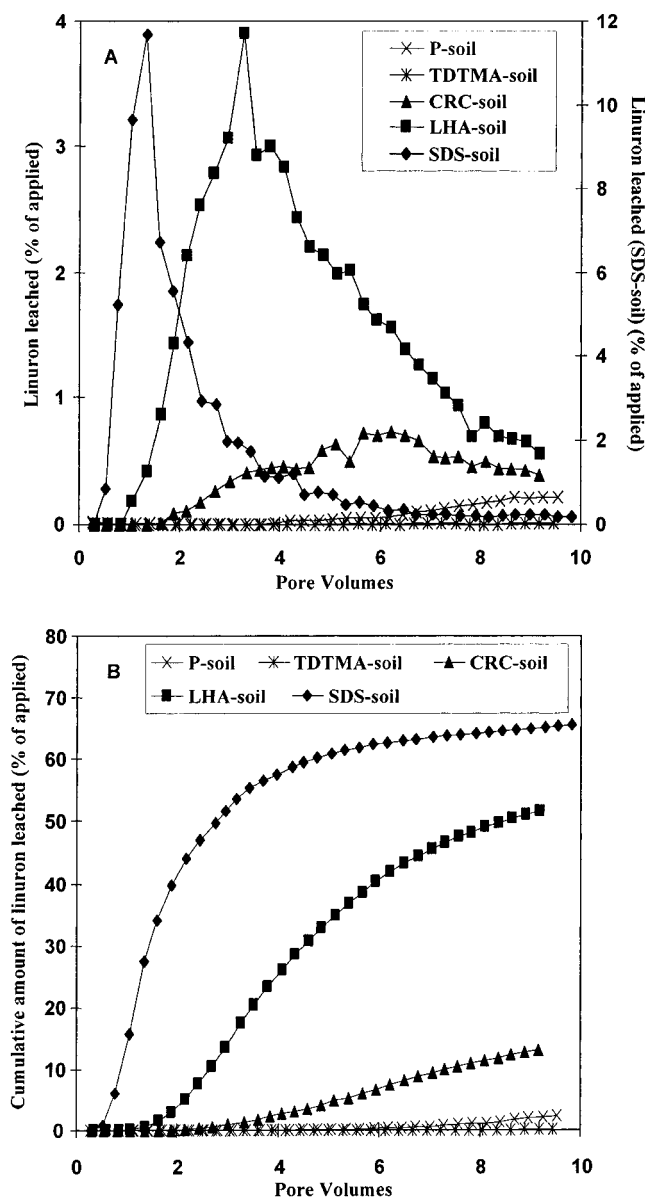
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Figure 3. Breakthrough (A) and cumulative (B) curves for linuron leaching in soil amended with 15 t ha^{-1} of the different organic matters and surfactants.

others; both the start of the herbicide leaching and the maximum of the curve are shifted to lower PV values than in unamended soil (0.53 PV and 1.35 PV).

The total amount of linuron leached in the column amended with LHA is almost identical to that leached in the column of unmodified soil, representing 51.3% of the linuron applied to the column, and decreases in the columns amended with CRC, P, and TDTMA. In the column amended with the latter compound, the linuron leached represents only 0.13% of the amount of the compound added to the column. By contrast, the amount of linuron leached in the column amended with SDS is greater than that leached from the natural soil and represents 65.4% of the herbicide applied. The retardation factor R, defined as the number of pore volumes necessary to leach 50% of the herbicide added to the columns (Brusseau and Rao, 1989), was 9.04 for the leaching of linuron in natural soil and 2.75 and 8.46 PV for the leaching of the herbicide in the soils amended with 15 t ha^{-1} of SDS and LHA, respectively. In the leaching of linuron in the soil amended with CRC, P,

and TDTMA, not even a 50% leaching of the herbicide was attained with the 9.5 PV used in the experiment. In the soils modified with these amendments the percentages leached with 9.5 PV were 13% (CRC), 2.29% (P), and 0.13% (TDTMA).

These results are consistent with those reported in an earlier study by the authors (Iglesias-Jiménez et al., 1997) on the adsorption of linuron by one soil modified with the same amendments as those used here at a dose of 20 t ha^{-1}. The Freundlich K adsorption constants varied inversely to the percentages of herbicide leached in soil columns in this study: SDS < LHA < soil < CRC < P < TDTMA.

Regarding the distribution of residual linuron (Table 5) in the columns amended with LHA and with SDS, an increase in the different segments with the depth is seen, together with a strong accumulation in the first segment in the columns amended with CRC, P, and TDTMA.

The results suggest that linuron is adsorbed by the OM of the amendments, giving rise to a change in the leaching kinetics of the herbicide and in the mass transfer as a function of the nature of the amendments and of the origin and doses of organic C added. Although the three organic amendments (P, LHA, CRC) have humic and fulvic acids in their composition (Diaz-Marcote, 1995; Liñan, 1998), there are important differences among them that account for their different effects on the adsorption of linuron and hence its leaching. P and CRC are solid amendments while LHA is a liquid amendment in which part of the OM is in solution and the other in suspension. When this substance is added to the soil, one fraction is incorporated into the adsorbent complex and the other remains in soluble form. The adsorption of linuron by this latter fraction, with a large adsorption capacity for hydrophobic organic compounds (Chiou, 1989; Santos-Buelga et al., 1992), is responsible for the greater degree of leaching of the herbicide. The humic acid-like substances of CRC are highly aliphatic in nature and different in structure from soil humic compounds, with an elevated presence of *n*-alkanes and fatty acids (González-Vila and Martín, 1985). On the other hand, TDTMA is an organic cation and hence is adsorbed via ion exchange by soil colloids.

As regards the adsorption capacity of humic and fulvic acids and TDTMA with respect to hydrophobic compounds such as linuron, it should be recalled that both types of acids, while hydrophobic, contain polar groups (OH, COOH) that endow them with a certain polar character, whereas TDTMA contains a completely hydrophobic long alkyl chain in its structure. The increased adsorption capacity of hexadecyltrimethylammonium (HDTMA) relative to soil organic matter was demonstrated by Sánchez-Camazano and Sánchez-Martín (1994) in an adsorption study of a hydrophobic organophosphorus insecticide (azinphos-methyl) by two soils with the same organic content but of different origins as well as by a humic acid. The organic matter in one of the soils was that naturally present in it while in the other it was the result of saturation with HDTMA. The organic matter from HDTMA was found to adsorb azinphos-methyl 20 times more efficiently than the OM occurring naturally in the soil and 10 times more efficiently than the humic acid tested. Boyd et al. (1988) also found organic matter from HDTMA in soils saturated with the cation to be 30 times more efficient

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than the soil organic matter for drawing benzene, dichloroethane, and perchloroethane from an aqueous solution.

The very marked changes in linuron leaching in the presence of SDS is due to the increase in the solubility of hydrophobic organic compounds in the presence of anionic surfactants. This aspect has been well documented for aromatic hydrocarbons by several authors (Valsaraj et al., 1988; Edwards et al., 1991), who attributed such changes to the adsorption of these compounds via hydrophobic bonds by the hydrophobic part of monomeric molecules or by the hydrophobic nucleus of surfactant micelles. For the 2 t ha^{-1} dose of SDS applied to the column, the compound is in monomeric form if its critical micellar concentration and the volume of water applied to the column are taken into consideration and it does not affect the leaching of linuron. However, at concentrations above the CMC, as is the case of the soil solution following the addition of the high SDS dose (15 t ha^{-1}), the surfactant molecules group to form micelles with a hydrophobic inner core and a hydrophilic external part. The great adsorbing capacity of the hydrophobic core for linuron causes the pesticide to be leached very strongly. The results of the present work are consistent with those obtained in a previous study by the authors (Iglesias-Jiménez et al., 1996) concerning the adsorption by soils of selected pesticides from aqueous solutions in the presence of SDS concentrations lower, equal to, or higher than the CMC. The Freundlich K constant for the adsorption of a hydrophobic organophosphorus insecticide (diazinon) was found to decrease with the rise in the concentration of surfactant in solution, K reaching a value of zero for a concentration of SDS in solution equal to 20 times the CMC of the compound.

The total balance of linuron recovered in the columns and leachates in general ranges between 63% and 69% of that applied, indicating that part of the herbicide must remain in the soil in a form that cannot be extracted by methanol. In the column amended with CRC, only 45% of the compound applied was recovered. In this case, in the extracts from the different segments of the column HPLC revealed the presence of the metabolite of linuron (*N*-3,4-dichlorophenyl)-*N*-methoxyurea), pointing to the effect of the strong microbial activity of CRC (Rothwel and Hortenstine, 1969; Perucci, 1990) in the degradation of the herbicide.

CONCLUSIONS

The content of organic matter is the most important parameter involved in the adsorption of linuron by soils. With an OM content above 2%, this parameter accounts for 98% of the variance in the herbicide adsorption. In soils with an OM content below 2%, the influence of the OM in adsorption is less marked, the content in silt plus clay exerting a stronger effect. According to the results of the study on linuron mobility by soil TLC, even though the herbicide is slightly mobile in soils with medium and high OM contents, it may be moderately mobile when the soils have a low OM content. The simultaneous presence in the soils of exogenous OM in the form of humic amendment and surfactants can alter the leaching kinetics and mass transfer of linuron as a function of the characteristics of the amendments and of the doses added. Additionally, these results point to the possibility of increasing or decreasing the leaching of hydrophobic pesticides in a controlled way through the addition of humic amendments or surfactants at selected doses. Also, the present data are of great interest as regards the potential use of such compounds in physicochemical methods aimed at preventing the pollution of waters and remediating soils and sediments polluted by hydrophobic pesticides. However, it should be noted that the use of surfactants for these ends requires much research aimed at selecting the most suitable surfactants and the most appropriate doses that will in each case (soil-pesticide) allow maximum efficiency with minimum cost.

ABBREVIATIONS USED

OM, organic matter; LHA, liquid humic amendment; P, peat; CRC, city refuse compost; TDTMA, tetradecyltrimethylammonium; SDS sodium dodecylsulfate; CMC, critical micellar concentration.

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