

Modification of clay barriers with a cationic surfactant to improve the retention of pesticides in soils

M.S. Rodríguez-Cruz^a, M.J. Sánchez-Martín^{a,*}, M.S. Andrades^b, M. Sánchez-Camazano^a

^a Instituto de Recursos Naturales y Agrobiología de Salamanca, CSIC, Salamanca, Spain

^b Dpto. Agricultura y Alimentación, Universidad de La Rioja, Logroño, Spain

Received 12 December 2005; received in revised form 2 May 2006; accepted 13 June 2006

Available online 16 June 2006

Abstract

In this work, the efficiency of reactive clay barriers in the immobilisation of organic pesticides in a sandy soil was studied. Reactive barriers were prepared by modification of montmorillonite, kaolinite and palygorskite clay minerals, and of a clayey soil with the cationic surfactant octadecyltrimethylammonium bromide (ODTMA). Percolation curves of the pesticides linuron, atrazine and metalaxyl of different hydrophobic character, were obtained in columns packed with a natural sandy soil with these barriers intercalated under saturated flow conditions. The cumulative curves in the unmodified soil indicated a leaching of pesticides greater than 85% of the total amount of compound added. After barrier intercalation, the breakthrough curves (BTC) indicated a dramatic decrease in the amounts of linuron leached in all columns and a significant modification of the leaching kinetics of atrazine and metalaxyl. Retardation factors, R , of the pesticides in the columns were significantly correlated with the organic matter content (OM) derived from the ODTMA of the organo clay/soil barriers ($r^2 \geq 0.78$). Significant correlations were also found between these R factors and the pore volume values corresponding to the maximum peaks of the BTCs ($r^2 = 0.83$; $p < 0.01$) or the total volumes leached ($r^2 = 0.44$; $p < 0.05$) for the pesticides atrazine and metalaxyl. The results obtained point to the interest in the use of reactive clay barriers for almost complete immobilisation of hydrophobic pesticides or for decreasing the leaching of moderately hydrophobic pesticides coming from point-like sources of pollution. These barriers would avoid the generation of elevated concentrations of these compounds in the soils due to their rapid washing.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Pesticides; Leaching; Soil column; Reactive barrier; Organo clay; Organo soil

1. Introduction

The important technological problems involved in the restoration of aquifers polluted by organic compounds have been well documented in recent years [1] and this has led to increasing interest in the development of low-permeability containment barriers and of high-permeability reactive barriers for the prevention of pollution [2,3]. This is specially the case of zones exposed to point-like sources of contamination by spills, illegal tipping, etc. Studies carried out on both types of barriers have included designs in which sorption is the main mechanism used to reduce pollutant flow. Accordingly, the characterisation of the sorption capacity of a material used as a barrier is a priority task. In this sense, laboratory assays in columns are an attractive means to accomplish this goal, despite the great difficulty some-

times involved in obtaining breakthrough curves when strong sorbent materials are used [4].

Low-permeability barriers such as soil/bentonite slurry walls are widely used to restrict the migration of mobile subsurface pollutants. Compacted clay liners are also used in municipal landfills to prevent the migration of contaminated fluid from the landfill to the groundwater. These liners can be constructed from clayey or silty clay soils, either natural or mixed with bentonite if necessary to meet the hydraulic conductivity requirements [5]. There are no specific requirements for soils to be used in bentonite-soil liners. Any type of soils can be used but the amount of bentonite is different. In general, the amount of bentonite used is generally less than 6% on a dry weight basis for soils with a broad range of grain size, and 10–15% for uniformly sized-sands [6]. Slurry walls may be effective at containing mainly polar organic pollutants for decades, although some investigators observed that breakthrough of these pollutants may occur due to molecular diffusion over a 5–30-year period [4,7].

* Corresponding author. Tel.: +34 923 219606; fax: +34 923 219609.
E-mail address: mjesusm@usal.es (M.J. Sánchez-Martín).

Permeable reactive barriers offer an *in situ* semi-passive remediation technology that uses materials which produce chemical or biochemical reactions to transform or immobilise pollutants. This method thus involves the emplacement of a semi-permeable reactive medium in the path of the flow of a pollutant plume [3]. Since the plume moves through the barrier, the pollutant is transformed into non-toxic or immobile products. Accordingly, it is necessary to assess the reactive materials based on its availability to transform or immobilise the pollutant at sufficient speed and on the possibility of maintaining adequate permeability during long periods of time and of releasing only compounds that are compatible with the environment as sub-products of the process.

Clay minerals are natural materials with a high capacity to adsorb organic compounds via different mechanisms of interaction. These minerals can be used, alone or mixed with soil, as barriers against organic pollutants. Such barriers are mainly reactive for positively charged organic pollutants (cation exchange) and for polar pollutants (ion-dipole bonds). However, they are less efficient at decreasing the transport of hydrophobic organic pollutants, which are mainly adsorbed by organic materials (hydrophobic bonds). For the adsorption of the latter compounds, it is necessary to modify natural clay barriers with organic additives that will transform them into reactive clays for such compounds. In this sense, some additives used are activated carbon, peat, city refuse compost, wood fibers or surfactants [3,8–11]. Cationic surfactants or quaternary ammonium salts with a long hydrocarbon chain are of special interest because their adsorption by clays leads to the formation of organo clays that are highly reactive for retaining hydrophobic compounds that are not retained by natural clays [12–17]. The carbon content provided by the surfactant means that a partition of the hydrophobic compounds in the organo clay occurs, the irreversibility of the compounds adsorbed being variable as a function of the clay mineral and of the hydrophobicity of the organic compound [15,17].

In the present work, we studied the immobilisation of organic pesticides in a sandy loam soil by the intercalation of reactive barriers of clays and of a clayey soil, both of them modified with octadecyltrimethylammonium bromide (ODTMA). The aim was to gain insight into the efficiency of these barriers in the immobilisation of pesticides with different hydrophobicity. The work was carried out in soil columns using different clays (montmorillonite, kaolinite and palygorskite) and different pesticides (linuron, atrazine and metalaxyl) with a view to shedding light on the influence of the structure of the clay mineral and of the hydrophobicity of the pesticide in the immobilisation process.

The study was conducted with the consideration that many pesticides are, to a greater or lesser extent, hydrophobic compounds and that many of them are often found in groundwaters [18–20]. Additionally, some investigations performed in recent years [21,22] have indicated that point-like sources of pollution may contribute, to a greater extent, to increasing the pollution of waters than diffuse contamination of the soil brought about by the use of pesticides in agricultural practices. The emplacement of a barrier of sorbent material in such zones could be a strategy for isolating the pesticides preventing the pollution from extending to soils or waters in the zone and/or allowing the natural degradation of these compounds immobilised *in situ*.

2. Materials and methods

2.1. Chemicals

Pesticides linuron, atrazine and metalaxyl were supplied by Riëdel de Haën (Hannover, Germany) (>98.5% purity). These compounds are solids with water solubility and log K_{ow} value of 81 $\mu\text{g}/\text{mL}$ and 3.00 for linuron, of 30 $\mu\text{g}/\text{mL}$ and 2.50 for atrazine, and of 8400 $\mu\text{g}/\text{mL}$ and 1.75 for metalaxyl [23]. The cationic surfactant, octadecyltrimethylammonium bromide (ODTMA), was supplied by Sigma–Aldrich (Madrid, Spain).

2.2. Soils and clays

Two soils from the province of Salamanca (Spain) were selected for this study. Soil samples were collected from the surface layer (0–30 cm depth). Some of their characteristics are included in Table 1. Soil A is a sandy loam soil and was used to study pesticide leaching in soil columns. Soil B is a sandy clay soil and was used to prepare the modified soil barrier. The soil samples collected were air dried and sieved (<2 mm). The pH of the soils was determined in water/soil suspensions (ratio 1/1) and the particle size distribution was determined using the pipette method [24]. The clay minerals (<1 mm) used in the study to prepare the modified clay barriers were Tidinit montmorillonite (M) (Morocco), Cuenca kaolinite (K) (Spain), and Bercimuel palygorskite (P) (Spain). These minerals were used with their impurities since it was of interest for their possible use to know their properties and behaviour as marketed. Their characteristics are included in Table 2.

The cation exchange capacity (CEC) of the soils and clays was determined by the ammonium acetate method [25]. Organic carbon (OC) contents were determined using an elemental carbon analyser (Wösthoff Carmograph 12 H Omega, Bochum, Germany), and the results were multiplied by 1.72 to express

Table 1
Characteristics of natural and modified soils studied

Soil	Texture	pH	CEC (cmol/kg)	OM (%)	Clay (%)	Silt (%)	Sand (%)	Clay mineralogy ^a
Soil A	Sandy loam	6.0	4.80	0.85	11.8	13.6	74.5	9 I–2 K
Soil B	Sandy clay	7.0	20.5	1.79	38.1	5.8	56.1	11 M–23 I–4 K
ODTMA–soil B			–	7.19	–	–	–	–

M: montmorillonite; I: illite; K: kaolinite.

^a Minerals in soils (%).

Table 2
Characteristics of natural and organo clays studied

Clay	CEC (cmol/kg)	OC (%)	OM (%)	Organic cation (cmol/kg)	Surface area (m ² /g)	d ₀₀₁ (Å)
Montmorillonite (M)	82	0.06	0.10	–	750	13.4
Kaolinite (K)	6.1	0.10	0.17	–	12	7.16
Paligorskite (P)	27	0.46	0.79	–	254	10.6
ODTMA-M	–	20.1	25.2	79.5	–	22.0
ODTMA-K	–	2.06	2.55	5.99	–	7.16
ODTMA-P	–	7.25	8.99	31.7	–	10.6

the OC as organic matter (OM) [25]. The clay minerals were identified by X-ray diffraction [26] using a Philips 1710 apparatus (Eindhoven, The Netherlands). Specific surface area was determined by the N₂ adsorption–desorption method at –196 °C on a Micromeritics Gemini analyser (Norcross, USA).

Clay minerals and Soil B were saturated with ODTMA by treating natural samples with a solution of ODTMA bromide in deionised water at temperature of 30 °C. Surfactant concentration was always lower than its critical micellar concentration (0.12 g/L) and we used a relation clay or soil/solution suitable to contain an amount of organic cation equivalent to 1.25 times the CEC of each sample [17,27]. The suspensions were shaken for 2 h and were subsequently centrifuged, washed with deionised water repeatedly until free of bromide ions as indicated by AgNO₃, freeze-dried and kept in an atmosphere at controlled humidity for later use. The carbon contents of the modified clays and soil were determined using the same carbon analyser as for natural samples. From this content the total OM content was calculated for each organo clay/soil (Tables 1 and 2).

2.3. Leaching experiment in soil columns

Experiments were performed in glass columns of 3 cm (i.d.) × 20 cm (length). Initially, the leaching of pesticides was carried out in columns packed with 100 g of natural soil A. Then, each column was over-saturated with water and allowed to drain the excess of water freely for 24 h so that humidity conditions were equivalent to field capacity. The pore volume (PV) of the packed columns was estimated by the weight difference between water-saturated columns and dry columns. Immediately after this, 1 mL of a solution of linuron, atrazine or metalaxyl at 1000 µg/mL in methanol was added to the top part of those columns saturated with water. Methanol was rapidly evaporated and so the three pesticides were incorporated to the soil in similar conditions [28,29]. Each experiment was carried out in triplicate. The columns were then washed by continuously applying 500 mL (70 cm) of water under a saturated flow regime. During the leaching experiment, the top of the column was in permanent contact with water pumping with a peristaltic pump Gilson Minipuls 3 (Gilson Inc. Middleton, WI, USA) to maintain saturated conditions. Fractions of leaching solution (15 mL) were collected successively and continuously using a Gilson F203 automated fraction collector (in which the concentrations of pesticides were measured).

Next, leaching of pesticides in the soil A with the organic barrier intercalated was carried out. The barriers were prepared

by incorporating in the upper part of the column an amount of organo clay/soil that would permit the OM content to be increased but would maintain the hydraulic conductivity of the column. According to these conditions, we used 10 g of natural soil A with 20% of ODTMA-M, 50% of ODTMA-K or 50% of ODTMA-P, or 10 g of ODTMA-soil B to prepare the different barriers. The OM content of these barriers increased the OM content of the natural soil by 9-, 2.6-, 8- and 12-fold, respectively. A control experiment was also carried out to study the leaching of pesticides in columns loaded with soil A and natural clay barriers intercalated. These natural clay barriers were prepared with the same amount of clay than the organic clay barriers. Since it was not possible to maintain hydraulic conductivity of the columns in these conditions, we carried out the experiment using a suitable clay amount which allowed hydraulic conductivity of the column. According to this, natural clay barriers were prepared from 10 g of natural soil A and 2.5% of M clay, 10% of K clay or P clay.

After leaching of pesticides, the columns were cut into three segments and the soil contained in each segment was turned over and weighed. Triplicate 5 g soil samples were taken from each segment and were shaken for 24 h with 10 mL of methanol to determine the contents of pesticides. Triplicate 1 g soil samples were also taken from each segment to determine the OM content of untreated soil A and soil A with the organic barriers intercalated. It was only noted a slight decrease (<5%) in the OM content of different segments of soil columns with the barriers intercalated indicating that the ODTMA adsorbed by the organo clays/soil remained stable during the leaching process.

Conservative tracer transport, using chloride as an ion tracer (KCl), was implemented to describe the dispersive characteristics of the columns used for the pesticide transport studies. The amount of chloride ion applied was 47 mg (5 mL from a KCl solution of 20 g/L in water), and the water flow rate was the same as that used in the pesticide leaching studies. The chloride ion concentration was determined using a Metrohm Ion Chromatograph (Metrohm Ltd., Switzerland).

The determination of pesticides in the leached fractions and soil extracts was accomplished by HPLC. The apparatus used was a Waters chromatograph (Waters Assoc., Mildford, MA) equipped with a model 600E multisolvent delivery system attached to a model 717 autosampler, a model 996 photodiode array detector (DAD), a ZQ mass spectrometer detector (MS), and Empower software as the data acquisition and processing system. A Waters Symmetry C18 column (7.5 mm × 4.6 mm i.d., 3.5 µm) was used at ambient temperature and the mobile

Table 3
Adsorption constants of linuron, atrazine and metalaxyl by the natural soil (K_{soil}), natural clays, organo clays and organo soil (K_{barrier})^a

	Linuron	Atrazine	Metalaxyl
Soil A	1.60 (0.5) ^b	0.67 (0.1)	0.20 (0.1)
Natural M	2.36 (0.9)	10.1 (0.7)	1.27 (0.0)
Natural K	9.90 (1.4)	10.9 (0.8)	0.05 (0.0)
Natural P	5.17 (1.1)	8.53 (0.1)	2.49 (0.8)
ODTMA-M	1454 (28)	146 (6.2)	191 (6.0)
ODTMA-K	174 (0.8)	18.6 (0.8)	2.12 (1.9)
ODTMA-P	332 (13)	54.0 (6.5)	20.2 (9.4)
ODTMA–soil B	325 (17)	41.8 (6.1)	43.3 (0.3)

^a Adsorption constants taken from previous works by the authors [17,27].

^b Standard error of two replicates.

phase was 70/30 (acetonitrile/water). The flow rate of the mobile phase was 0.3 mL/min and the sample injection volume was 10 μ L. Detection by HPLC/DAD was at 210 nm for linuron, 220 nm for atrazine and 194 nm for metalaxyl and detection by HPLC/MS to confirm the identity of these compounds was carried out by monitoring the positive molecular ion (m/z) 249.1 for linuron, 216.7 for atrazine and 280.3 for metalaxyl.

2.4. Determination of retardation factors

Retardation factors, R , were determined as indicators of the shifts of the maximum peaks of breakthrough curves (BTC) for pesticide leaching in natural soil columns and in natural soil columns with intercalated barriers. These factors were calculated according to the expression proposed by Wagner et al. [30]: $R = 1 + K\rho((1 - \xi)/\xi)$, where R is the retardation factor, ρ the density of the soil (g/cm^3), ξ the porosity (pore volume in the packed bed divided by the total volume occupied by the packed bed), and K is the adsorption constant of pesticides by the column components.

K values were determined according to the equation proposed by Voudrias [31]: $K = \theta_{\text{soil}}K_{\text{soil}} + \theta_{\text{barrier}}K_{\text{barrier}}$, where θ_{soil} and θ_{barrier} are the respective fractions of natural soil and natural clay or organo clay/soil in the columns, and K_{soil} and K_{barrier} are the respective adsorption constants of linuron, atrazine and metalaxyl by the natural soil and by the different natural clays or organo clays/soil comprising the barriers of the columns. These adsorption constants (K_{soil} and K_{barrier}) are included in Table 3

Table 4
Parameters of soil columns, retardation factors (R), and adsorption constants (K)

Column	Column density (g/cm^3)	Column porosity (cm^3/cm^3)	Retardation factors			Adsorption constants ^a		
			Linuron	Atrazine	Metalaxyl	Linuron	Atrazine	Metalaxyl
Soil A	0.71	0.31	3.59	2.08	1.32	1.60	0.67	0.20
Soil A + M	0.71	0.27	4.08	2.33	1.39	1.61	0.69	0.20
Soil A + K	0.71	0.29	3.91	2.34	1.34	2.43	1.69	0.19
Soil A + P	0.71	0.28	3.93	2.34	1.40	1.96	1.46	0.43
Soil A + M-ODTMA	0.71	0.24	69.5	9.0	10.0	30.6	3.58	4.02
Soil A + K-ODTMA	0.71	0.23	25.7	4.79	1.72	10.2	1.57	0.30
Soil A + P-ODTMA	0.71	0.21	48.6	9.76	4.15	18.1	3.34	1.20
Soils A + B-ODTMA	0.71	0.26	68.7	10.5	10.0	33.9	4.78	4.51

^a Determined from adsorption constants of pesticides by different components of soil columns according to Voudrias [31].

and they were taken from previous works by the authors [17,27] where the adsorption of various pesticides by different natural and organo clays/soils, including those selected in this work, were studied from adsorption isotherms in batch experiments. Parameters of soil columns and values of adsorption constants (K) and retardation factors calculated are included in Table 4.

3. Results and discussion

3.1. Pesticide leaching in unmodified soil column

Fig. 1 shows the BTCs of linuron, atrazine and metalaxyl leaching with water, in the unmodified soil columns, and in soil columns with natural clay barriers intercalated. This figure also includes the BTC of the chloride tracer ion in the soil column. Chloride ion is a conservative ion and hence does not undergo retention or degradation in soils. It is considered as a water flow tracer in the soil columns [32,33]. In this work BTCs of chloride ion leaching begin at about 0.5 PV and reach a maximum at about 1 PV, as it is generally expected to occur in the percolation of conservative ions. This movement indicates that water flow on the used soil column is uniform and retardation factor R for chloride ion leaching is close to 1. According to this, differences in the leaching of pesticides with respect to the ion tracer leaching in similar soil columns should not be related to water flow [34].

The BTCs of atrazine and metalaxyl leaching in the unmodified soil were very similar, and they indicated a rapid leaching of the pesticides. The peak of maximum concentration of BTCs was found for a water volume of 1.1 PV (atrazine) and of 1.5 PV (metalaxyl). Additionally, the shape of the curves with short final tails could be considered similar to that found for conservative ion, indicating a weak interaction of both compounds with the adsorbent. The maximum concentration was almost identical for the two pesticides representing 29.3% for atrazine, and 30.2% for metalaxyl of the total mass fraction applied to the columns. The BTC of linuron leaching had an asymmetrical shape and a final tail, indicating a stronger interaction of this pesticide with the soil than that of atrazine and metalaxyl [35]. The BTC maximum appeared for a higher volume of water (2.57 PV) and the maximum concentration was lesser representing 10.9% of the mass fraction applied initially.

Table 5
Amounts of pesticides retained and leached (% of applied) in natural soil columns and in soil columns with intercalated ODTMA–clays and ODTMA–soil barriers

Segment (cm)	Soil A	Soil A + ODTMA-M	Soil A + ODTMA-K	Soil A + ODTMA-P	Soil A + ODTMA–soil B
Linuron					
0–5 cm	1.61 (0.13) ^a	94.2 (2.75)	82.2 (4.33)	96.2 (1.10)	92.3 (7.51)
5–10 cm	1.76 (0.37)	0.67 (0.06)	2.40 (0.82)	0.55 (0.07)	0.51 (0.13)
10–15 cm	2.18 (0.64)	0.59 (0.09)	1.61(0.34)	0.00 (0.00)	1.52 (1.61)
Total soil	5.55 (0.44)	95.5 (2.98)	86.2 (3.36)	96.7 (0.31)	94.3 (6.14)
Total leached	85.9 (2.58)	1.83 (0.31)	3.75 (0.34)	0.11 (0.02)	0.42 (0.18)
Maximum peak concentration	10.9 (0.66) (2.57VP)	–	–	–	–
Atrazina					
0–5 cm	0.53 (0.03)	1.34 (0.16)	0.25 (0.16)	1.10 (0.78)	469 (4.57)
5–10 cm	0.07 (0.01)	0.35 (0.11)	0.10 (0.09)	0.98 (0.21)	4.27 (0.09)
10–15 cm	0.48 (0.21)	0.51 (0.11)	0.12 (0.11)	1.10 (0.19)	5.27 (0.44)
Total soil	1.08 (0.06)	2.26 (0.11)	0.47 (0.25)	3.18 (1.14)	56.4 (4.22)
Total leached	109 (6.85)	101 (8.49)	108 (6.55)	88.1 (2.16)	47.2 (1.73)
Maximum peak concentration	29.3 (1.18) (1.10 VP)	4.87 (0.37) (6.95 VP)	7.62 (0.33) (3.61 VP)	6.03 (0.37) (8.76 VP)	2.72 (0.28) (12.1 VP)
Metalaxyl					
0–5 cm	1.23 (0.84)	13.6 (3.42)	1.20 (0.31)	1.60 (1.40)	33.2 (6.75)
5–10 cm	0.80 (0.02)	1.07 (0.01)	0.14 (0.12)	0.05 (0.03)	0.50 (0.00)
10–15 cm	2.34 (0.95)	1.07 (1.01)	0.23 (0.15)	1.72 (0.05)	0.72 (0.11)
Total soil	4.37 (1.25)	15.4 (3.72)	1.36 (0.51)	1.72 (0.35)	34.5 (6.86)
Total leached	88.7 (15.3)	80.8 (2.16)	101 (0.95)	97.4 (3.51)	54.8 (4.39)
Maximum peak concentration	30.2 (5.24) (1.50 VP)	4.23 (0.17) (5.64 VP)	8.00 (0.09) (1.75 VP)	8.97(0.54) (4.85 VP)	2.17 (0.07) (6.41 VP)

^a Standard error of three replicates.

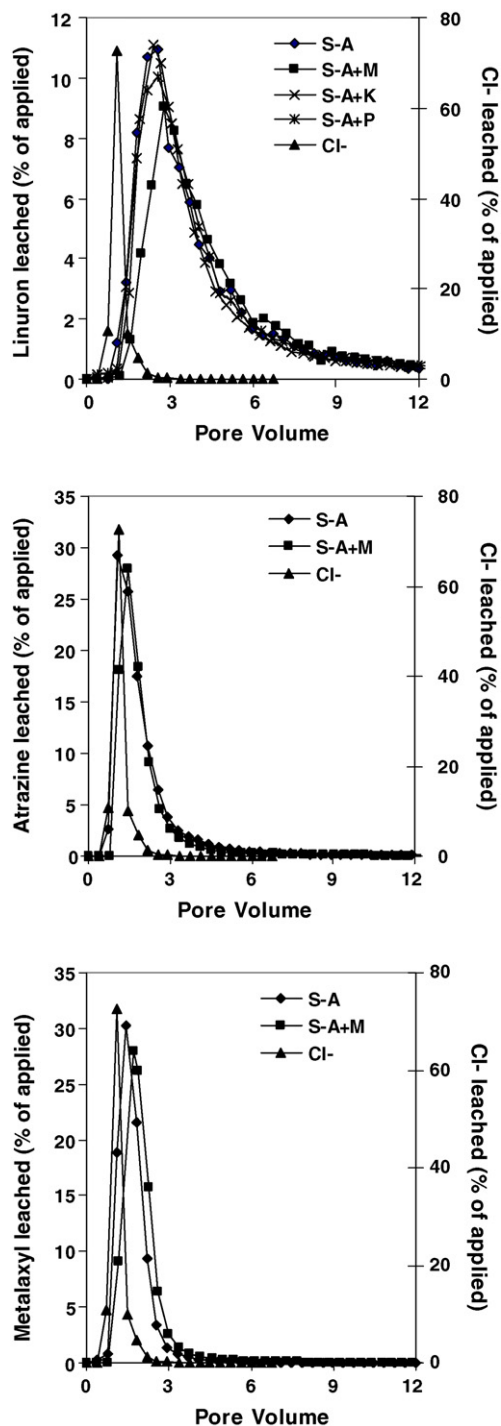


Fig. 1. Breakthrough curves for leaching of linuron, atrazine and metalaxyl in unmodified soil columns and in soil with natural clay barriers intercalated.

The total amounts leached and the residual amounts in the column after leaching expressed as percentages of the amount initially added to the column are shown in Table 5. The leaching of the three pesticides in soil A (sandy loam) was almost complete after the application of 500 mL of water to the column and the residual amount of each of them was shared equally along the three segments of the column (Table 5).

The values of R factors calculated for leaching of pesticides in unmodified soil column (Table 4) are in agreement with the

PV values corresponding to the maximum peaks. The highest R value corresponds to linuron owing to the greater adsorption of this pesticide by soil A than that of atrazine or metalaxyl. Differences in the mobility of these pesticides in soils of different composition and with an OM content <2% have also been reported by several authors in studies carried out using soil thin layer chromatography. These pesticides were defined as slightly mobile (linuron) [12], moderately mobile (atrazine) [36] and very mobile (metalaxyl) [37].

Leaching of the three pesticides in soil columns with natural clay barriers intercalated using a suitable clay amount which allowed hydraulic conductivity of the column were also carried out (see Section 2.3). The BTCs of atrazine and metalaxyl leaching were similar to those of unmodified soil when K and P clays were used in the barriers (results not shown), and were nearly similar when M clay was used (Fig. 1). In this last case, the concentration of maximum peak decreased slightly and it was similar for the two herbicides (27.9% of the total mass fraction applied). This maximum peak was found for a greater water volume than in unmodified soil columns, at 1.5 PV for atrazine and 1.7 PV for metalaxyl. BTCs of linuron leaching were also similar to that of unmodified soil if K clay was used as a barrier, but when barriers were prepared with natural P or M clays (Fig. 1) a delay of the BTC (M-barrier) and a decrease of the maximum peak concentration were observed. These concentrations were 10.0% and 9.04% of the total mass fraction applied in the columns with P and M clays intercalated, respectively.

The values of R factors for leaching of pesticides in soil columns with natural clay barriers intercalated were also calculated (Table 4). They increased slightly comparing with unmodified soil and they are in agreement with the PV values corresponding to the maximum peaks. The total amounts leached and the residual amounts in the column after leaching were similar to those obtained in unmodified soil (data not shown).

Although this experiment cannot be used as a control of that with organic barriers intercalated as it was indicated previously, the results obtained provided useful information about the use of natural clay barriers. Thus, the low or null effect of these barriers in the leaching of used pesticides indicated that the natural clays have limitations to be used as barriers in order to decrease the leaching of the pesticides studied or other compounds with similar properties in soils.

3.2. Pesticide leaching in soil column with intercalated barriers

Figs. 2–4 show the BTCs and cumulative curves of linuron, atrazine and metalaxyl leaching with water in the columns of soil A with intercalated barriers of the clay minerals or of soil B modified with ODTMA. In principle, the BTCs obtained indicate a different behaviour of the pesticides in the natural soil and in the soil with intercalated barriers. Differences in the BTCs corresponding to leaching of the different pesticides were also observed in all systems. The BTC of the chloride tracer ion (not included) was almost identical for unmodified and modified soil columns.

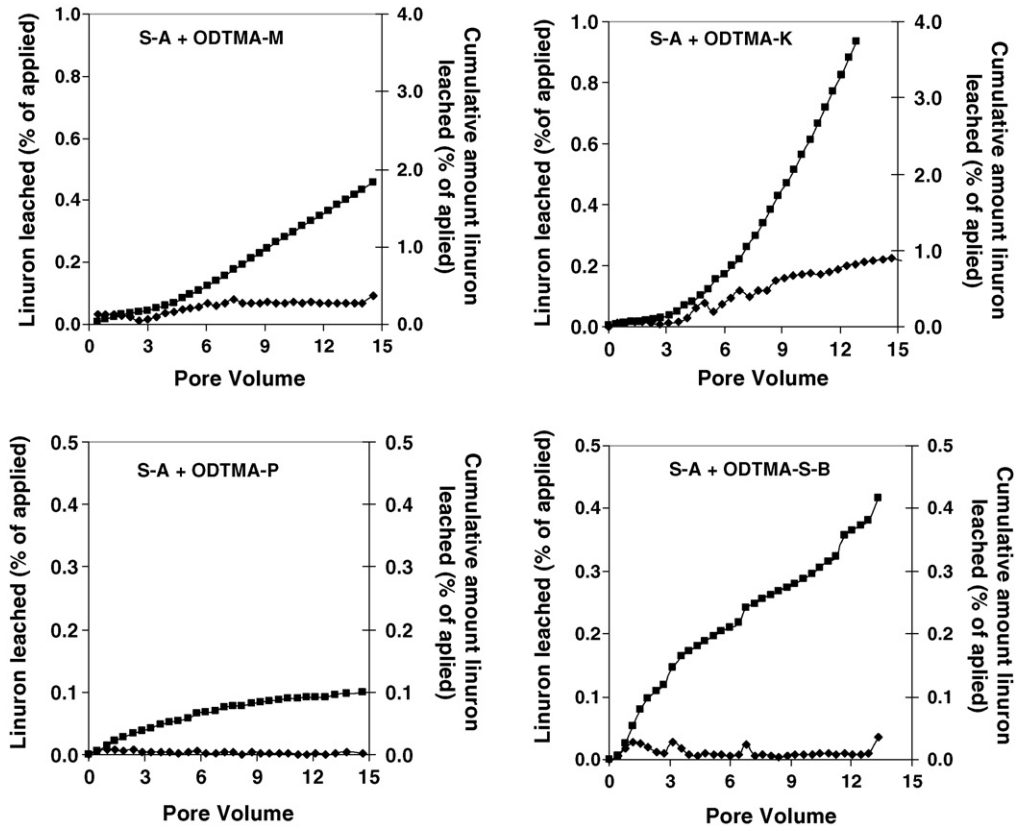


Fig. 2. Breakthrough and cumulative curves for linuron leaching in soil columns with organo clays/soil barriers intercalated.

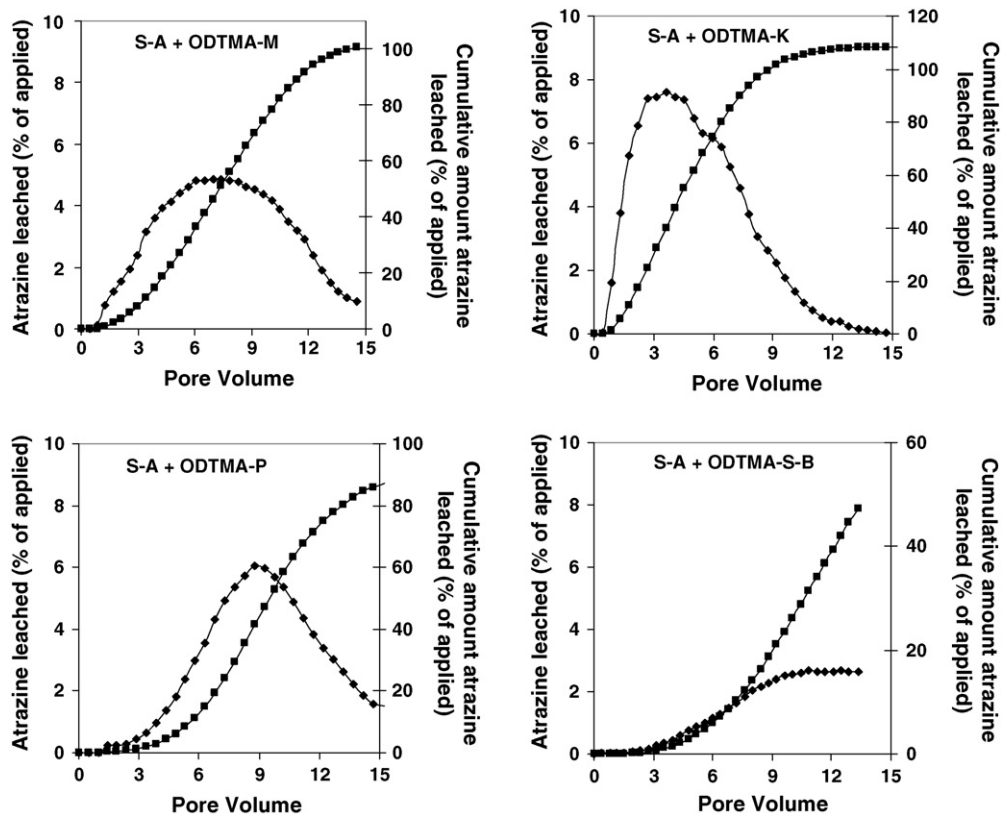


Fig. 3. Breakthrough and cumulative curves for atrazine leaching in soil columns with organo clays/soil barriers intercalated.

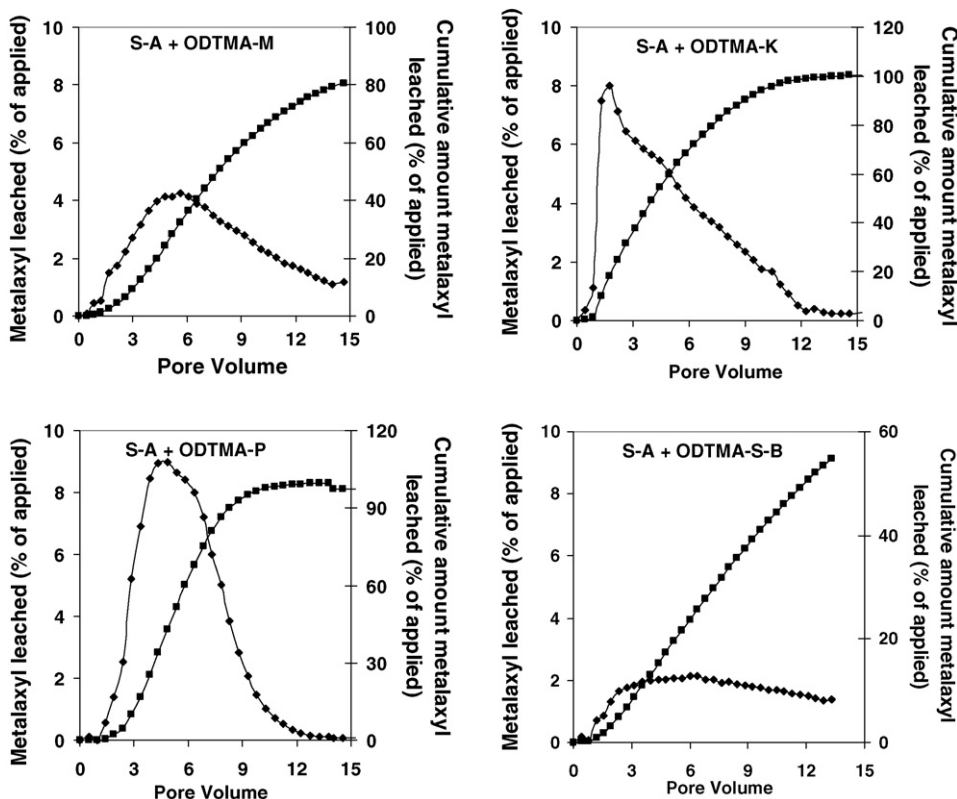


Fig. 4. Breakthrough and cumulative curves for metalaxyl leaching in soil columns with organo clays/soil barriers intercalated.

The BTCs of linuron leaching in the soil columns with intercalated barriers of organo clays/soil indicate a dramatic decrease in the leaching of the pesticide in all columns. The BTCs do not show a maximum peak with the flow of water added. Accordingly, the maximum must occur at a PV value above 12–15, depending on the column characteristics. The values of R factors calculated for leaching of linuron in soil columns with intercalated barriers (Table 4) are very high and vary between 69.5 (column with ODTMA-M barrier) and 25.7 (column with ODTMA-K barrier). The total amounts of linuron leached in the modified columns expressed as percentages of the initial amount added (Table 5) were very low and varied between 0.11% and 3.75% when barriers of ODTMA-P and ODTMA-K were intercalated, respectively. The percentages of residual linuron in the columns varied between 86.2% and 96.7%, indicating the almost complete retention of the compound in the first segment of the columns. The results obtained indicate an almost complete immobilisation of linuron in the columns of soil with intercalated barriers of organo clays/soil after the application of 500 mL of water under saturated flow regime. The immobilisation is due to the increase in the adsorption of linuron by the soil, in turn due to the presence of materials enriched in OM derived from ODTMA.

The intercalation of organo clay/soil barriers in the soil columns did not give rise to the complete immobilisation of atrazine or metalaxyl, which are less hydrophobic pesticides than linuron. However the BTCs obtained indicated an important modification in the leaching kinetics of these pesticides and a much slower washing process than in the natural soil. In gen-

eral, the leaching BTCs of these pesticides are not symmetrical, but instead have tails, indicating a continuous washing of the compound as from the maximum peak corresponding to the slower adsorption–desorption kinetics of the compound [35,38]. The BTCs of atrazine leaching in columns with ODTMA-M, ODTMA-K and ODTMA-P barriers (Fig. 3) show peaks toward the 3.61–8.76 PV zone, and the maximum concentrations attained represent 4.87%, 7.62% and 6.03%, respectively of the amount of atrazine initially added. These values indicate a decrease of between four- and five-fold of the maximum concentration obtained in the natural soil. The BTC of atrazine leaching with ODTMA–soil B was different, a maximum peak was not achieved with the total flow of water added, instead, a plateau was obtained whose maximum concentration represented 2.72% of the amount initially added.

The BTCs of metalaxyl leaching in the columns with organo clay barriers (Fig. 4) show peaks with maximum concentrations representing 4.23% (ODTMA-M), 8.00% (ODTMA-K) and 8.97% (ODTMA-P) of the amount initially added. These concentrations indicate a decrease of between four- and seven-fold the maximum peak concentration in the column of natural soil. In the columns with the ODTMA–soil B barrier, a slow and continuous leaching of the compound was seen, and a plateau maximum was also reached after the addition of total water volume, which represents 2.17% of the compound initially applied. The total amounts of atrazine and metalaxyl leached in columns with intercalated barriers of organo clays were similar to those obtained in the columns of untreated soil, and they were close to 50% of that added initially when the barrier of organo soil B was

intercalated (Table 5). However, intercalation of ODTMA–clay barriers in the soil columns delayed the maxima of percolation curves and decreased the presence of both pesticides in the leachates to a significant extent.

The values of R factors calculated for leaching of atrazine and metalaxyl in soil columns with intercalated barriers (Table 4) are consistent with the parameters obtained in the leaching experiments in the different columns as regards the PV of the maximum peak of BTCs and the total amounts leached in the columns. A highly significant linear correlation was found between the R factors and the PV of the maximum peaks corresponding to BTCs of atrazine and metalaxyl ($r^2 = 0.83$; $p < 0.001$) and a negative significant correlation was also obtained between the R factors and the total volumes leached ($r^2 = 0.44$; $p < 0.05$).

On the other hand a linear correlation can also be established between the R factors and the OM content of the barriers for each pesticide. A significant correlation coefficient was found for linuron ($r^2 = 0.91$; $p < 0.01$), and for the pesticides atrazine and metalaxyl, with lesser hydrophobic character, correlation coefficients with a lower degree of significance than for linuron were also found ($r^2 = 0.78$; $p < 0.05$ for atrazine, and $r^2 = 0.84$; $p < 0.05$ for metalaxyl). These results indicate an increase of the R factors with the OM content of barriers independent of the clay mineral in which the OM derived of ODTMA is supported. However considering that the OM content (as organic cation) supported by each clay depends on its structural properties, it will be necessary to take into account the type of clay mineral to be used in order to add the appropriate amounts of these materials in the preparation of an effective reactive clay barrier. Therefore a decreasing in the leaching of pesticides in a controlled way would be possible.

4. Conclusions

The results obtained indicate the efficiency of the intercalation of clay/soil barriers modified with the cationic surfactant ODTMA in decreasing the mobility of linuron, atrazine and metalaxyl in a sandy loam soil. The BTCs of pesticide leaching point to the almost complete immobilisation of linuron, the most hydrophobic pesticide, and a decrease in the leaching kinetics of the less hydrophobic pesticides atrazine and metalaxyl after application of 500 mL of water to the columns with intercalated barriers. The maximum concentrations of the BTCs decreased 4–10-fold for atrazine and 3–14-fold for metalaxyl with respect to the maximum concentrations obtained in the unmodified soil. The retardation factors, R , calculated for leaching of pesticides in the soil columns increased in the range 3.59–69.5 (linuron), 2.08–10.5 (atrazine), and 1.32–10.0 (metalaxyl) when the organic barriers were intercalated in the columns of the natural soil. Significant correlations found between these R factors and the OM content (as organic cation) of the intercalated barriers indicated that these factors were independent of the type of the clay mineral in which this OM is supported. Accordingly, reactive clay barriers of the three clay minerals studied in this work could be used taking into account that the required amount of each one will depend on the OM content (as organic cation) supported by these clays. These results highlight

on the interest in sorption barriers to decrease the leaching of pesticides of different hydrophobicity from point-like sources of pollution, preventing the generation of elevated concentrations caused by a rapid washing of the pesticide.

Acknowledgements

This work was funded in Spain by the “Ministerio de Ciencia y Tecnología” and the “Junta de Castilla y León” as part of Projects REN2000-0884/TECNO and CSI15-03, respectively. The authors thank L.F. Lorenzo, J.M. Ordax, and A. Nuñez for technical assistance.

References

- [1] National Research Council, Alternatives for Groundwater Cleanup, National Academy Press, Washington, DC, 1994.
- [2] M.M. Scherer, S. Richter, R.L. Valentine, P.J.J. Alvarez, Chemistry and microbiology of permeable reactive barriers for *in situ* groundwater clean up, Crit. Rev. Environ. Sci. Technol. 30 (2000) 363–411.
- [3] K.L. Roehl, T. Meggyes, F.G. Simon, D.I. Stewart, Long-Term Performance of Permeable Reactive Barriers, Elsevier, Amsterdam, 2005.
- [4] A.J. Rabideau, J.V. Benschoten, A. Khandelwal, C.R. Repp, Sorbing vertical barriers, in: J.A. Smith, S.E. Burns (Eds.), Physicochemical Groundwater Remediation, Kluwer Academic Press, New York, 2001, pp. 115–138.
- [5] S. Kumar, W.L. Yong, Effect of bentonite on compacted clay landfill barriers, Soil Sediment Contam. 11 (2002) 71–89.
- [6] D.E. Daniel, Case histories of compacted clay liners and covers for waste disposal facilities, in: Proceedings of the Third International Conference on Case Histories in Geotechnical Engineering, St. Louis, MO, 1993, pp. 1407–1425.
- [7] C.D. Shackelford, Diffusion of contaminants through waste containment barriers, Transport. Res. Record 1219 (1989) 169–182.
- [8] M.I. Selim, J. Wang, Fate of atrazine in biologically active granular activated carbon, Environ. Toxicol. Chem. 13 (1994) 3–8.
- [9] E. Iglesias-Jiménez, E. Poveda, M.J. Sánchez-Martín, M. Sánchez-Camazano, Effect of the nature of exogenous organic matter on pesticide sorption by the soil, Arch. Environ. Contam. Toxicol. 33 (1997) 117–124.
- [10] M. Sánchez-Camazano, E. Iglesias-Jiménez, M.J. Sánchez-Martín, City refuse compost and sodium dodecyl sulphate as modifiers of diazinon leaching in soil, Chemosphere 35 (1997) 3003–3012.
- [11] M. Sánchez-Camazano, M.J. Sánchez-Martín, R. Delgado-Pascual, Adsorption and mobility of linuron in soils as influenced by soil properties, organic amendments, and surfactants, J. Agric. Food Chem. 48 (2000) 3018–3026.
- [12] S. Xu, G. Sheng, S.A. Boyd, Use of organoclays in pollution abatement, Adv. Agron. 59 (1997) 25–62.
- [13] M. Sánchez-Camazano, M.J. Sánchez-Martín, Organo-clays as adsorbents for azinphosmethyl and dichlorvos in aqueous medium, Water Air Soil Pollut. 74 (1994) 19–28.
- [14] S.M. Kop, J.B. Dixon, Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene, Appl. Clay Sci. 18 (2001) 111–122.
- [15] L. Groisman, C. Rav-Acha, Z. Gerstl, U. Mingelgrin, Sorption of organic compounds of varying hydrophobicities from water and industrial wastewater by long- and short-chain organoclays, Appl. Clay Sci. 24 (2004) 159–166.
- [16] M.J. Carrizosa, P.J. Rice, W.C. Koskinen, I. Carrizosa, M.C. Hermosín, Sorption of isoxaflutole and DKN on organoclays, Clays Clay Miner. 52 (2004) 341–349.
- [17] M.J. Sánchez-Martín, M.S. Rodríguez-Cruz, M.S. Andrades, M. Sánchez-Camazano, Efficiency of different clay minerals modified with a cationic surfactant in the adsorption of pesticides. Influence of clay

- type and pesticide hydrophobicity, *Appl. Clay Sci.* 31 (2006) 216–228.
- [18] D. Barcelo, S. Chiron, A. Fernandez-Alba, A. Valverde, M.F. Alpendurada, Monitoring pesticides and metabolites in surface waters and groundwaters in Spain, in: M.T. Meyer (Ed.), *Herbicides-Metabolites in Surface and Groundwater*, American Chemical Society, Washington, 1996.
- [19] R.F. Spalding, M.E. Exner, D.D. Snow, D.A. Cassada, M.E. Burbach, S.J. Monson, Herbicides in groundwater beneath Nebraska's management systems evaluation area, *J. Environ. Qual.* 32 (2003) 92–99.
- [20] M. Sánchez Camazano, L.F. Lorenzo, Atrazine and alachlor inputs to surface and groundwaters in irrigated corn cultivation areas of Castilla-León region, Spain, *Environ. Monit. Assess.* 105 (2005) 11–24.
- [21] A. Carter, How pesticides get into water—and proposed reduction measures, *Pestic. Outlook* 11 (2000) 149–152.
- [22] K. Müller, M. Bach, H. Hartmann, M. Spiteller, H.G. Frede, Point- and nonpoint-source pesticide contamination in the Zwester Ohm catchment, Germany, *J. Environ. Qual.* 31 (2002) 309–318.
- [23] C. Tomlin, *The Pesticide Manual*, British Crop Protection Council, Cambridge, UK, 2000.
- [24] P.R. Day, *Methods of Soil Analysis*, American Society of Agronomy, Madison, 1965.
- [25] M.L. Jackson, *Soil Chemical Analysis*, Prentice Hall, Englewood Cliffs, New York, 1958.
- [26] G. Brown, G.W. Brindley, X-ray diffraction procedures for clay mineral identification, in: G.W. Brindley, G. Brown (Eds.), *Crystal Structures of Clay Minerals and their X-Ray Identification*, Mineralogical Society, London, 1980, pp. 305–359.
- [27] M.S. Rodríguez-Cruz, M.J. Sánchez-Martín, M.S. Andrades, M. Sánchez-Camazano, Comparison of pesticide sorption by physicochemically modified soils with natural soils as a function of soil properties and pesticide hydrophobicity, *Soil Sediment Contam.* 15 (2006) 401–415.
- [28] K. Li, B. Xing, W.A. Torello, Effect of organic fertilizers derived dissolved organic matter on pesticide sorption and leaching, *Environ. Pollut.* 134 (2005) 187–194.
- [29] R. Cherrier, A. Boivin, C. Perrin-Ganier, M. Schiavon, Sulcotrione versus atrazine transport and degradation in soil columns, *Pest Manage. Sci.* 61 (2005) 899–904.
- [30] J. Wagner, H. Chen, B.J. Brownawell, J.C. Westall, Use of cationic surfactants to modify soil surfaces to promote sorption and retard migration of hydrophobic organic compounds, *Environ. Sci. Technol.* 28 (1994) 231–237.
- [31] E.A. Voudrias, The concept of a sorption chemical barrier for improving effectiveness of landfill liners, *Water Manage. Res.* 20 (2002) 251–258.
- [32] J.W. Biggar, D.R. Nielsen, Miscible displacement. II. Behaviour of tracers, *Soil Sci. Soc. Am. Proc.* 126 (1962) 125–128.
- [33] K. Tilahun, J.F. Botha, T.P. Bennie, Transport of bromide in the Bainsvlei soil: field experiment and deterministic/stochastic model simulation. I. Continuous water application, *Aust. J. Soil Res.* 43 (2005) 73–80.
- [34] L. Sánchez, E. Romero, A. Peña, Ability of biosolids and a cationic surfactant to modify methidathion leaching. Modelling with pescol, *Chemosphere* 53 (2003) 843–850.
- [35] W.A. Jury, H. Fluhler, Transport of chemicals through soils: mechanisms, models and field applications, *Adv. Agron.* 47 (1992) 141–201.
- [36] T. Crisanto, M.J. Sánchez Martín, M. Sánchez Camazano, M. Arienzo, Mobility of pesticides in soils. Influence of soil properties and pesticide structure, *Toxicol. Environ. Chem.* 45 (1994) 97–104.
- [37] M.S. Andrades, M.J. Sánchez-Martín, M. Sánchez-Camazano, Significance of soil properties in the adsorption and mobility of the fungicide metalaxyl in vineyard soils, *J. Agric. Food Chem.* 49 (2001) 2363–2369.
- [38] A.J. Beck, A.E.J. Johnston, K.C. Jones, Movement of non ionic organic chemicals in agriculture soils, *Crit. Rev. Environ. Sci. Technol.* 23 (1993) 219–248.