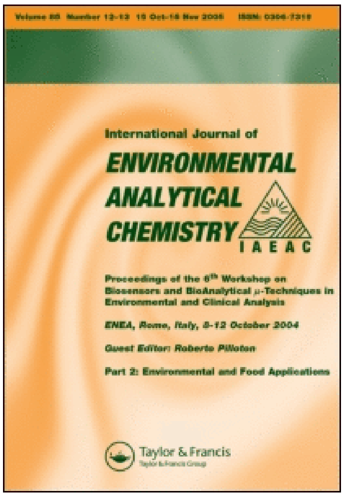

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Clay-Herbicide Complexes to Retard Picloram Leaching in Soil

Rafael Celis; Carmen HermosÍN; Luis Cornejo; JosÉ Carrizosa; Juan Cornejo

To cite this Article Celis, Rafael , HermosÍN, Carmen , Cornejo, Luis , Carrizosa, JosÉ and Cornejo, Juan(2002) 'Clay-Herbicide Complexes to Retard Picloram Leaching in Soil', International Journal of Environmental Analytical Chemistry, 82: 8, 503 — 517

To link to this Article: DOI: 10.1080/03067310290018785

URL: http://dx.doi.org/10.1080/03067310290018785

Intern. J. Environ. Anal. Chem., Vol. 82, No. 8–9, pp. 503–517

Taylor & Francis
Taylor & Francis Group

CLAY–HERBICIDE COMPLEXES TO RETARD PICLORAM LEACHING IN SOIL

RAFAEL CELIS*, Mª CARMEN HERMOSÍN, LUIS CORNEJO,
Mª JOSÉ CARRIZOSA and JUAN CORNEJO

Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC,
Avda Reina Mercedes 10, Apdo 1052, 41080 Sevilla, Spain

(Received 24 August 2001; In final form 6 February 2002)

An approach for minimizing the risk of ground water contamination for highly mobile pesticides is to enhance the soil sorption process through the application of the pesticide together with a sorbent which limits the amount of pesticide immediately available for undesirable leaching losses. In this work, a number of clays exchanged with different inorganic and organic cations were assayed as sorbents of the acidic herbicide picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid) and the ability of three selected clays to retard the release of picloram into water and to reduce picloram leaching through a soil column was investigated. For the selected clays, Fe^{3+}-saturated Wyoming montmorillonite (Fe-SW), octadecylammonium-treated Arizona montmorillonite (ODA-SA_1) and hexadecyltrimethylammonium-saturated Arizona montomorillonite (HDTMA-SA_2), two types of clay–picloram complexes (a physical mixture, PM, and a strongly-sorbed complex, SC) were prepared. All clay–picloram complexes yielded slow release of the herbicide and retarded its vertical movement through soil columns compared to the free technical compound, showing that clay–pesticide complexes prepared from selectively-modified clays may be useful in reducing rapid leaching of highly mobile pesticides such as picloram.

Keywords: Herbicide; Leaching; Organoclays; Picloram; Slow release

INTRODUCTION

The environmental problems associated with the use of highly mobile pesticides are a current issue because these compounds are increasingly being detected in ground and surface waters. Anionic pesticides are a particular concern because they are very weakly retained by most soil and sediment components and hence can rapidly move dissolved in the soil solution [1,2]. Recently, increasing attention is being directed to design strategies to reduce runoff and leaching of highly mobile pesticides in order to minimize the risk of water pollution.

The fact that most pesticide formulations in current use deliver the bulk, if not all, of the active ingredient in an immediately available form that is readily released to the environment increases the likelihood of ground water contamination by pesticides [3]. Many pesticides, for instance, are applied to the field as soluble liquids, which increases the risk of vertical movement if heavy rain events occur shortly after application, before

---

*Corresponding author. Fax: +34-954-624002. E-mail: rcelis@irnase.csic.es

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310290018785

pesticide molecules have time to diffuse into soil aggregates and reach sorption sites in soil colloids [4]. In this context, an approach for minimizing the risk of ground water contamination for highly mobile pesticides is to enhance the soil sorption process through the application of the pesticide together with a carrier which limits the amount of pesticide immediately available for undesirable leaching losses. Among the various materials proposed as pesticide carriers, recently there has been renewed interest in the use of natural soil constituents, such as clays, iron oxides or humic acids [3,5–9]. Clays are particularly interesting due to their low cost, ubiquitous occurrence in nature, and the possibility to selectively modify their surfaces, for instance by incorporating large organic cations in the interlayers, to improve their affinity for selected pesticides [8–12].

In this work, the acidic herbicide picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid) was used as a model of highly mobile pesticide to investigate the ability of selectively-modified clays to retard the release of the herbicide into water and to reduce herbicide leaching in soil. Picloram is a systemic herbicide commonly used to control deeply rooted herbaceous weeds and woody plants in forestry, rangelands, pastures, and small grain crops [13,14]. Its anionic character at the pH of most soil and water environments ($pK_a = 2.3$) results in very low sorption on soil particles and in turn in an extremely high soil mobility [14]. Picloram sorption has been shown to be poorly correlated with soil clay content, but significantly correlated to soil organic matter content [15,16]. It has also been shown that picloram is preferentially sorbed in the molecular form and that sorption is increased with decreasing pH [17]. At typical soil pH (5–9), however, the anionic form of picloram comprises greater than 99% of the dissolved chemical, which explains the low sorption of this herbicide by most soils. Picloram is stable to hydrolysis and anaerobic degradation, and degrades very slowly in aerobic conditions with half-lives ranging from 167 to 513 days depending on soil type [14]. Because of its low sorption and its long soil persistence, its major route of dissipation appears to be leaching and a number of studies have reported its appearance in ground water at significant levels [14,18–21]. In fact, according to the USEPA [14], the principal environmental risks of picloram relate to contamination of surface and ground water, and damage to nontarget terrestrial plants including crops adjacent to areas of application via runoff or leaching. In addition, there is also concern related to endangered terrestrial mammals and endangered aquatic animals [14].

The specific objectives of this work were: (i) to evaluate the sorption–desorption of picloram by two montmorillonites previously treated with different inorganic and organic cations in order to provide the clay surfaces with sorptive properties and (ii) to test the ability of clays displaying different sorption affinities for picloram to slow the release of the herbicide into water and to retard herbicide leaching through soil columns compared to the free technical compound. Fourier-transform infrared spectroscopy was used to establish the clay–herbicide interaction mechanisms and to interpret herbicide leaching results.

EXPERIMENTAL

Materials

The clays used in this study were Na-Wyoming montmorillonite, SWy-2, and Ca-Arizona montmorillonite, SAz-1, supplied by the Source Clays Repository

TABLE I Characteristics of inorganic and organic clays and Freundlich coefficients for picloram sorption*

Sorbent abbreviation	*Montmorillonite*	*Main interlayer cation*	*OC (%)*	*OCtS (%)*	d_{001} *(nm)*	K_f	N_f	R^2
Fe-SW	SWy-2	Fe^{3+}	–	–	1.25	68 ± 1	1.60 ± 0.09	0.99
HDTMA-SW_1	SWy-2	HDTMA	9.8	56	1.75	7 ± 1	1.13 ± 0.19	0.95
HDTMA-SW_2	SWy-2	HDTMA	14.7	85	1.82	37 ± 1	0.63 ± 0.05	0.98
ODA-SW_1	SWy-2	ODA	9.9	60	1.71	13 ± 3	1.35 ± 0.41	0.79
ODA-SW_2	SWy-2	ODA	15.0	90	1.71	62 ± 1	1.45 ± 0.11	0.98
HDTMA-SA_1	SAz-1	HDTMA	15.0	54	2.20 p	40 ± 1	1.09 ± 0.07	0.99
HDTMA-SA_2	SAz-1	HDTMA	22.5	83	2.40	240 ± 1	0.48 ± 0.05	0.97
ODA-SA_1	SAz-1	ODA	17.2	67	3.10 p	175 ± 1	1.37 ± 0.07	0.99
ODA-SA_2	SAz-1	ODA	25.5	98	3.70 p	504 ± 2	1.68 ± 0.16	0.97

*ODA: octadecylammonium; HDTMA: hexadecyltrimethylammonium; OC: organic carbon; OCtS: percentage of the CEC of the clay occupied by organic cations (calculated from the organic C content); d_{001}: basal spacing; p: poorly defined; K_f, N_f: Freundlich coefficients for picloram sorption ± standard error; R^2: regression coefficient for the Freundlich-fit sorption isotherm.

(Clay Minerals Society, Columbia, MO). The cation exchange capacities (CEC) of SWy-2 and SAz-1 are 76 and 120 $cmol_c\,kg^{-1}$, respectively, being the result of isomorphic substitutions in the octahedral layer. Fe^{3+}-saturated Wyoming montmorillonite (FeSW) was obtained by treating 10 g of SWy-2 with 100 mL of a 1 M solution of $FeCl_3$. After treatment (24 h, three times), the solid was washed with distilled water until Cl-free, and then lyophilized. For the preparation of the clays exchanged with alkylammonium cations, 10 g of SWy-2 or SAz-1 were treated with 100 mL of an ethanol : water (1 : 1) solution containing an amount of alkylammonium (chloride salt) equal to either 50% or 100% of the CEC of the clay. The suspensions were shaken for 24 h, centrifuged, washed with distilled water until Cl-free, and then lyophilized. The abbreviations used to refer to the different clays prepared together with their main physicochemical properties are summarized in Table I.

The picloram used in this study was the analytical grade compound (purity 97.5%) provided by Dr. Ehrenstorfer Lab. (Germany). The soil used in the leaching experiments was a sandy-clay soil (0–20 cm) classified as Typic Rhodoxeralf with 70% sand, 10% silt and 20% clay (12% illite, 4% kaolinite and 4% montmorillonite). It has 0.99% organic matter and 1.04% Fe_2O_3. The pH measured in a 1 : 2 (w : w) solid : deionized water suspension was 7.9.

Sorption–Desorption Experiments

Picloram sorption–desorption isotherms were obtained by the batch equilibration technique using 50 mL polypropylene centrifuge tubes. Initial picloram solutions were prepared in distilled water at concentrations (C_{ini}) ranging from 50 to 1000 μM. Duplicate 20 mg sorbent samples were equilibrated with 8 mL of picloram initial solutions by shaking mechanically at 20 ± 2°C for 24 h. After equilibration, the suspensions were centrifuged and the equilibrium concentrations (C_e) determined in the supernatant solutions by high performance liquid chromatography (HPLC). The amount of herbicide sorbed (C_s) was calculated from the difference between the initial (C_{ini}) and the equilibrium (C_e) solution concentrations. Preliminary experiments showed that picloram did not sorb on the walls of the centrifuge tubes and that 24 h was sufficient to obtain picloram sorption equilibrium on ODA-SA_1, which was the clay displaying the greatest sorption–desorption hysteresis. Desorption was measured immediately after sorption from the highest concentration point of the sorption isotherm. The 4 mL of supernatant removed for the sorption analysis were replaced with 4 mL distilled water. The samples were resuspended, shaken for another 24 h, centrifuged and equilibrium concentration in the supernatant was determined. This desorption cycle was repeated three times. Sorption and desorption isotherms were fit to the logarithmic form of the Freundlich equation: $\log C_s = \log K_f + N_f \log C_e$, where C_s (mmol kg^{-1}) is the amount of herbicide sorbed at the equilibrium concentration C_e (mmol L^{-1}), and K_f and N_f are the empirical Freundlich constants. Hysteresis coefficients, H, for the sorption–desorption isotherms were calculated according to: $H = N_{f\text{-des}}/N_f$, were N_f and $N_{f\text{-des}}$ are the Freundlich N_f constants obtained for the sorption and desorption isotherms, respectively [22,23].

Fourier-Transform Infrared Spectroscopy

Clay samples containing an amount of picloram sorbed high enough to allow analysis by Fourier-transform infrared (FT-IR) spectroscopy were prepared by five successive treatments of the clays (20 mg) with a 1 mM picloram solution (8 mL). Controls (treated with water) and picloram-treated samples were washed once with deionized water, air-dried, and analyzed as KBr disks in a Nicolet 5PC FT-IR spectrometer.

Preparation of Clay–Picloram Complexes used in the Release and Leaching Experiments

Two types of clay–picloram complexes were prepared with the selected sorbents (Fe-SW, ODA-SA$_1$ and HDTMA-SA$_2$): (i) a physical mixture (PM) was obtained by thoroughly mixing 40 mg of technical grade picloram with 960 mg of clay without solvent addition; (ii) a more intimate association (SC) was prepared by adding 10 mL of methanol to 1 g of PM, shaking for 24 h, and then air-drying. The amount of picloram in the complexes corresponded to a 4% content in active ingredient (a.i.). All solids were thoroughly ground in an agate mortar and stored at 4°C until used. Previous work had shown that the organic solvent used in the preparation of SC formulations favors the clay–herbicide interaction, making the release of the herbicide slower compared to PM [8]. It appeared that the organic solvent facilitated the diffusion of the herbicide within the clay aggregates, favoring retention and/or trapping of the herbicide during methanol evaporation. On the basis of these results, we expected different rates and extents of picloram release from the two types of formulations prepared.

Release Study

Two milligram of picloram (a.i.), as clay complex or technical product, were added to 250 mL distilled water in glass bottles lined with screw caps. At selected times after herbicide application (from 0 to 144 h), the bottles were hand-shaken, allowed to settle for 10 min, and then 2 mL of the supernatant solution was filtered and picloram concentration determined by HPLC. The periodical removal of such a small amount of supernatant was assumed not to have any influence on the release pattern. Picloram release kinetics was obtained in duplicate.

Column Leaching Experiment

Leaching was studied in 30 × 5 cm methacrylate columns made up of six 5 cm-long sections sealed with silicon, which also helped minimize preferential flow along the walls of the columns. The top ring was filled with sea sand and the bottom ring with sea sand plus glass wool, to prevent losses of soil and contamination of leachates with soil particles. The other four rings were hand-packed with 490 g of air-dried soil, then saturated with 300 mL 0.01 M $CaCl_2$ and allowed to drain for 24 h. The calculated pore volume of the columns after saturation was 200 ± 20 mL. The amount of picloram corresponding to an application rate of $\sim 4\,kg\,ha^{-1}$ (0.85 mg a.i.) was applied to the top of duplicate soil columns as free-technical compound (dissolved in 5 mL water) or as clay complexes. This application rate is within the range of 2.2–9.5 kg ha^{-1} recommended for field application of picloram [24]. The columns were leached with 0.01 M $CaCl_2$ at a rate of 50 mL day^{-1}. The leachates were collected daily and the concentration of picloram determined by HPLC until the herbicide concentration measured was less than 0.1 μM.

Herbicide Analysis

Picloram analysis was performed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The following conditions were used: Novapack C18 column (150 mm length × 3.9 mm i.d.), 25 : 75 methanol:diluted phosphoric acid (pH = 2.0) eluent mixture at a flow rate of 1 mL min^{-1}, 25 μL injection volume, and UV detector at 225 nm. External calibration curves with standard solutions between 1 and 1000 μM were used in the calculations.

RESULTS AND DISCUSSION

Picloram Sorption on Clays

Picloram sorption isotherms an all sorbents assayed fit the Freundlich equation with $R^2 > 0.95$ (Table I). The only exception was the sorption isotherm on ODA-SW_1, which showed poor fitting to the Freundlich equation ($R^2 = 0.79$). While no measurable sorption of picloram was observed for the original montmorillonites (SWy-2 and SAz-1), the exchange of the original inorganic cations with ODA and HDTMA provided the resulting organoclays with sorptive properties. Saturation of SWy-2 with Fe^{3+} also resulted in considerable sorption of picloram by FeSW (Table I). Some sorption isotherms are upward sloping ($N_f > 1$), in particular those on ODA-organoclays and Fe-SW, but in general they were also well described by the Freundlich equation. Upward slopping sorption isotherms have been attributed to competition of the pesticide with water molecules for sorption sites [25,26], which agrees with the high hydrophilic character of Fe^{3+} and the monosubstituted ODA cation compared to the highly hydrophobic HDTMA cation.

The lack of sorption of picloram observed for SWy-2 and SAz-1 can be attributed to the anionic character of picloram ($pK_a = 2.3$) at the pH of the suspensions (pH > 6) and repulsion of the anionic species from the negatively charged clay surfaces. Negligible or even negative sorption by montmorillonite has previously been reported for other acidic pesticides, such as 2,4-D and imazamox [2,27,28]. The treatment of

SWy-2 and SAz-1 with the organic cations, HDTMA and ODA, increased the affinity of the clay surfaces for picloram and resulted in K_f values that ranged from 7, for HDTMA-SA$_1$, to 504, for ODA-SA$_2$. The ability of FeSW to sorb picloram ($K_f = 68$) can be attributed to the high surface acidity provided by the Fe^{3+} ions (suspension pH = 3), which promotes protonation of the pesticide molecules, thus reducing repulsion and favoring sorption [29].

Although no clear relationships could be found between sorption (K_f values) and the OC content or the basal spacing values of the organoclays, data in Table I show that SA-organoclays were clearly more sorptive than SW-organoclays with similar amounts of the same organic cation. The low-charge SW montmorillonite favors the horizontal arrangement of the alkyl chains of the organic cation in the interlayer ($d_{001} = 1.7$–1.8 nm, Table I), which is stabilized by hydrophobic interactions with noncharged regions of the clay surface [28]. In contrast, the proximity of two adjacent charges in SA montmorillonite promotes a vertical arrangement of the alkyl chains that results in high basal spacings of the resulting organoclays ($d_{001} > 2.2$ nm) [30,31]. It appears that the vertical arrangement of the organic cations in SA-organoclays makes the interlayer space more accessible for picloram molecules compared to the SW-organoclays, resulting in greater sorption. These results are similar to those of previous work where the interlayer thickness was responsible for difference in pesticide sorption by different organoclays [30,32,33].

Besides the interlayer thickness, the nature and amount of organic cation present in the organoclays also influenced picloram sorption. Thus, an increase in the organic cation saturation (OCtS) resulted in greater picloram sorption (Table I), which indicates the role of the organic cations in the sorption of picloram by the organoclays. In addition, higher K_f values were measured for clays exchanged with ODA compared to the same clays exchanged with similar amounts of HDTMA. These results are very similar to those reported by Celis *et al.* [28] for the acidic herbicide imazamox, and can be attributed to the possibility of polar interactions between the herbicide molecules and the monosubstituted amino group of ODA cations. Polar interactions should be significantly less important for HDTMA-organoclays due to the higher hydrophobicity of the tetrasubstituted amino group of HDTMA [28].

Sorbent Selection

Based on the sorption results, three clays varying in their affinity for picloram were selected to test their ability to retard the release of the herbicide into water and to reduce herbicide leaching losses. The three clays selected were Fe-SW ($K_f = 68$), ODA-SA$_1$ ($K_f = 175$) and HDTMA-SA$_2$ ($K_f = 240$). Picloram sorption–desorption isotherms on these clays are shown in Fig. 1, where not only the different sorption affinities, but also the different hysteresis of the sorption–desorption isotherms should be noted. Thus, hysteresis coefficients, H, calculated by dividing the desorption and adsorption Freundlich N_f values ($H = N_{f\text{-des}}/N_f$) were 0.75 for HDTMA-SA$_2$, 0.54 for Fe-SW and 0.44 for ODA-SA$_1$. The less sorptive clays, Fe-SW and ODA-SA$_1$, were therefore those displaying lower H values, i.e., greater hysteresis of the sorption–desorption process [22,23]. Possible causes for the observed sorption–desorption hysteresis include irreversible sorption of picloram and slow desorption kinetics for the sorbed species [2,23].

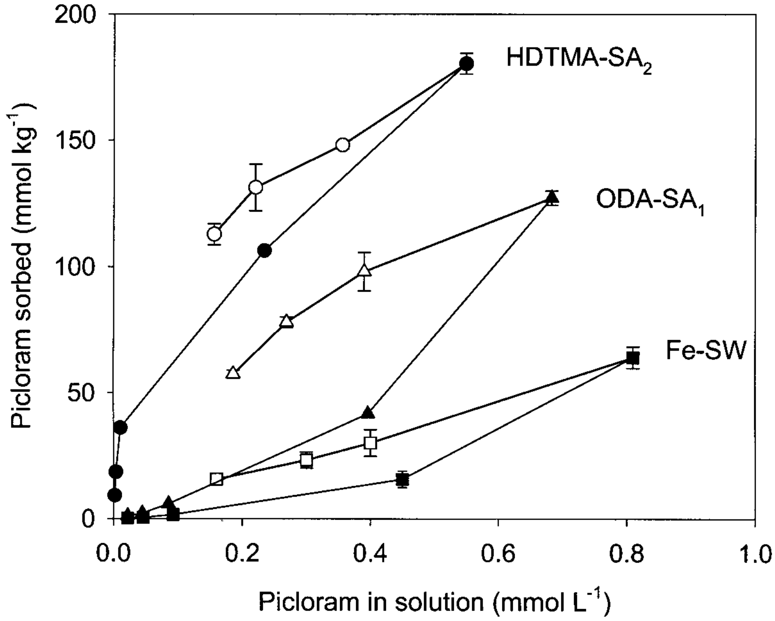

FIGURE 1 Picloram sorption–desorption isotherms on the three selected clays. Solid symbols are sorption points, whereas open symbols are desorption points.

FT-IR Spectroscopy Study

FT-IR spectra of HDTMA-SA$_2$, ODA-SA$_1$ and Fe-SW treated with picloram together with those of the untreated blank clay samples and pure picloram are shown in Fig. 2. Bands corresponding to picloram in the FT-IR spectra of the complexes revealed the presence of the herbicide sorbed on the clays. For all three clays, herbicide treatment led to a reduction in the intensity of the OH stretching vibration band (broad band at about 3400 cm^{-1}) corresponding to hydration water of the clay, strongly indicating that picloram sorption involved replacement of hydration water molecules at the clay surface.

The band at 1716 cm^{-1} in the FT-IR spectrum of HDTMA-SA$_2$ treated with picloram was assigned to the C=O stretching vibration of the protonated carboxylic group of the herbicide [34] and indicated that sorption of picloram on HDTMA-SA$_2$ involved the molecular (undissociated) form of the pesticide. Compared to the FT-IR spectrum of pure picloram, this band appeared slightly shifted to higher wavenumber (from 1710 to 1716 cm^{-1}) suggesting that interactions between the –COOH group of the herbicide and the clay surface were weaker compared with the intermolecular interactions occurring between the carboxylic and amino groups of the herbicide in the pure compound (Fig. 2c). The shifting of the N–H stretching vibration band (ν_{N-H}) of picloram from 3476 cm^{-1} to 3447 cm^{-1} upon sorption by HDTMA-SA$_2$ suggests relatively strong interaction between the $-NH_2$ group of the herbicide and the clay surface.

In contrast to HDTMA-SA$_2$, notably absent in the FT-IR spectra of Fe-SW and ODA-SA$_1$ treated with picloram (Figs. 2e and 2g) were bands corresponding to the protonated carboxylic group of the pesticide (especially the band at 1710 cm^{-1}),

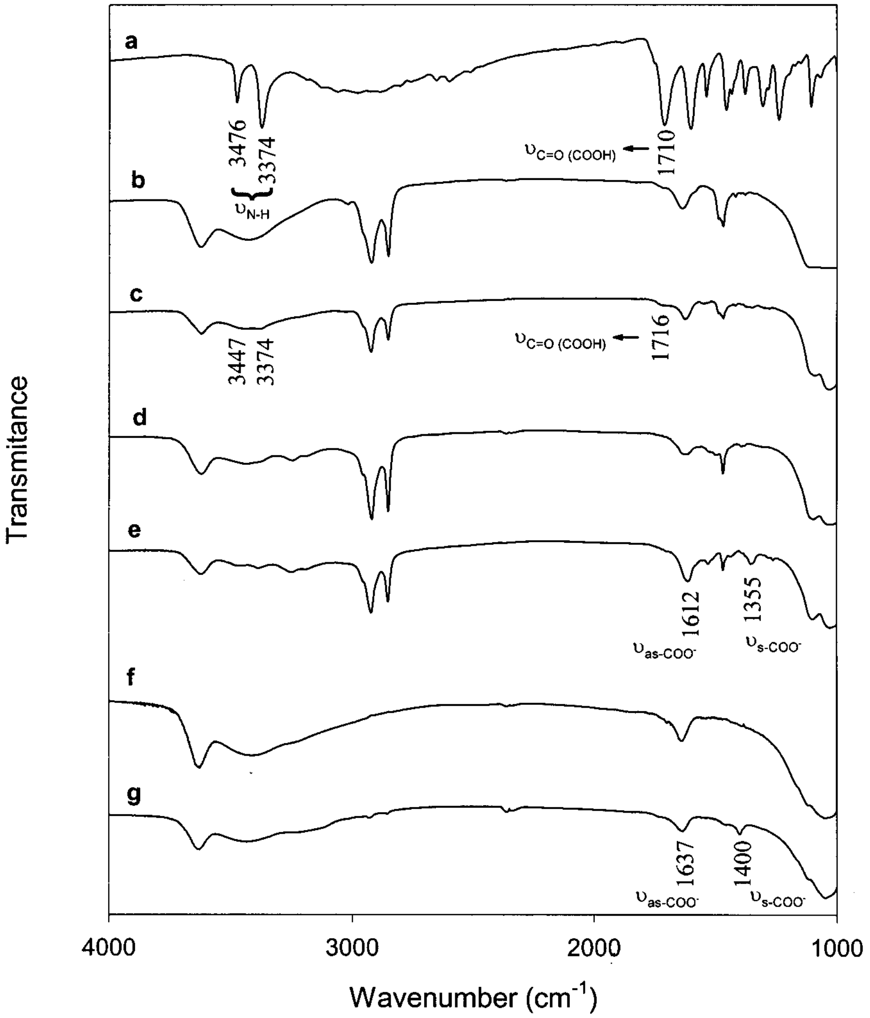

FIGURE 2 Fourier-transform infrared spectra of: (a) picloram; (b) HDTMA-SA$_2$; (c) HDTMA-SA$_2$ + picloram; (d) ODA-SA$_1$; (e) ODA-SA$_1$ + picloram; (f) Fe-SW and (g) Fe-SW + picloram.

accompanied by the appearance of bands corresponding to the anti-symmetrical (ν_{as-COO^-}) and symmetrical (ν_{s-COO^-}) vibration bands of the carboxylate anion (Fig. 2). Probably, the bending vibration of the – NH$_2$ group of picloram also contributed to the bands observed at 1612 cm^{-1} and 1637 cm^{-1} for ODA-SA$_1$ and Fe-SW, respectively. These results suggest at least partial ionization of the carboxylic group of picloram when interacting with Fe-SW and ODA-SA$_1$, most likely as a result of coulombic attraction between the ionized –COO$^-$ group of the herbicide and the interlayer cation of the clay. The different sorption mechanism derived from the FT-IR spectroscopy study for Fe-SW and ODA-SA$_1$ compared to HDTMA-SA$_2$ can be explained taking into the account the high polarizing power of the Fe^{3+} cations on one hand, and the higher hydrophilic character of ODA compared to HDTMA on the other, which may have resulted in contribution of ionic attraction mechanism to picloram sorption by Fe-SW and ODA-SA$_1$ [28]. In addition, reinforcement of the clay–herbicide binding by this ionic contribution to the sorption mechanism is consistent with the greater irreversibility of the sorption–desorption isotherms found for Fe-SW and ODA-SA$_1$ compared to HDTMA-SA$_2$ (Fig. 1).

Release Study

The release of picloram into water from clay complexes (PM and SC preparations) are compared in Fig. 3 with the release pattern of the free technical product. All clay complexes released the herbicide slower compared to the technical product. In contrast

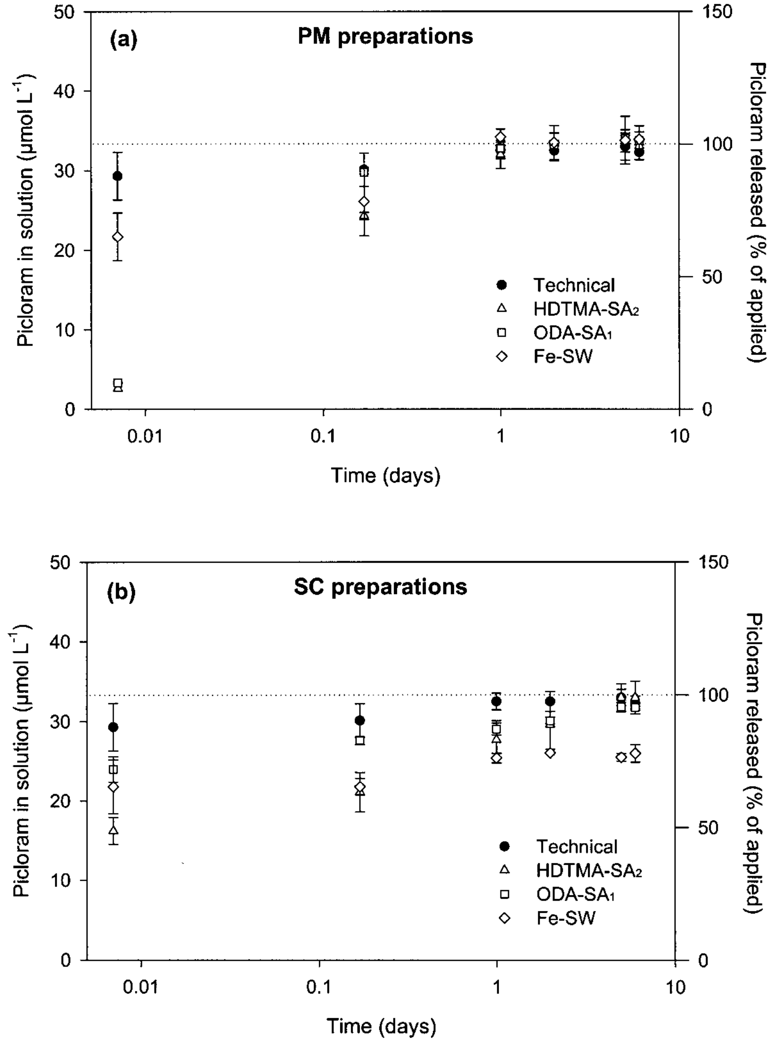

FIGURE 3 Picloram release kinetics in water from clay–herbicide complexes and for the free technical product: (a) PM preparations; (b) SC preparations.

to an immediate release of 90% of the herbicide for the technical product, the initial release for the complexes varied from 10% to 70% depending on the clay and the type of preparation. For the labile PM complexes, an inverse relationship was observed between the initial release and the affinities of the clays for picloram, i.e., Fe-SW (65%) > ODA-SA_1 (10%) $\geq$ HDTMA-SA_2 (9%), while the final release, reached at $t = 1$ day, was close to 100% in every case. For the SC preparations, the release equilibrium was reached slower (2–5 days) compared to the PM complexes, reflecting a more intimate association between the clays and the herbicide. Nevertheless, the final releases of picloram from SC preparations were high: 100% for HDTMA-SA_2 and ODA-SA_1, and 80% for Fe-SW. In summary, most of the herbicide was released into water from all clay–herbicide complexes, although at slower rate than that observed for the free technical compound.

Picloram release data were analyzed by applying the generalized model [6,8,35].

$$M_t/M_z = k \cdot t^n + c$$

where M_t/M_z is the percentage of pesticide released at time t and k, n and c are constants which are characteristic of the systems. These parameters are given in Table II for all clay–picloram complexes and for the technical compound. The lower c values obtained for the clay complexes compared to the free compound indicates reduced initial release ($t = 0$), while the different values of k and n depending on the formulation reveal that a range of rates and extents of picloram release occurred depending on the sorbent and the type of preparation. This suggests the possibility to select diverse preparations according to the intended use [6,8].

Column Leaching Study

Breakthrough curves (BTCs) for picloram applied to soil columns as free-technical compound and clay complexes are shown in Figs. 4, 5 and 6. The position of the maximum concentration peak (close to one pore volume), the symmetry of the breakthrough curve, and the total amount of herbicide recovered (~ 100%) for the free picloram application indicated very little retention and degradation of the herbicide in the soil column. This agrees with previous work reporting rapid leaching and long persistence of picloram in soil [16,36]. Compared to the technical compound, all clay–herbicide complexes reduced the maximum concentration peak of the BTC and extended the presence of the herbicide in the leachates at moderate concentrations up

TABLE II Constants from fitting the equation $M_t/M_z = k \cdot t^n + c$ to the release data of picloram in water for clay-based formulations and the free compound

Formulation	*c*	*k*	*n*	R^2
Free picloram	88 ± 2*	8 ± 3	0.22 ± 0.10	0.84
HDTMA-SA_2 (PM)	8 ± 6	83 ± 7	0.09 ± 0.03	0.98
ODA-SA_1 (PM)	10 ± 2	88 ± 2	0.04 ± 0.01	1.00
Fe-SW (PM)	65 ± 7	29 ± 8	0.18 ± 0.10	0.88
HDTMA-SA_2 (SC)	48 ± 3	32 ± 4	0.29 ± 0.05	0.98
ODA-SA_1 (SC)	73 ± 1	16 ± 1	0.23 ± 0.02	1.00
Fe-SW (SC)	65 ± 4	86 ± 5	0.29 ± 0.78	0.78

*Value ± standard error.

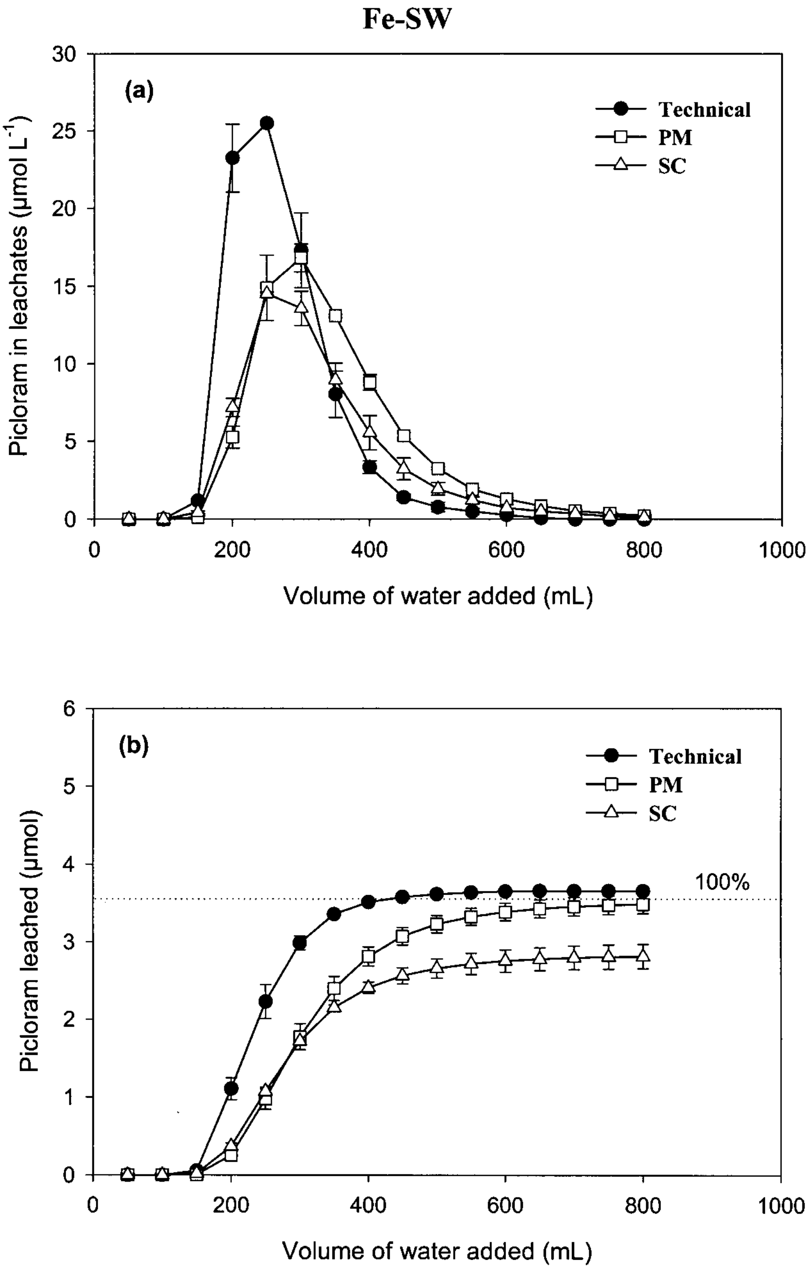

FIGURE 4 Picloram BTCs after application to soil columns as free technical product and Fe-SW complexes: (a) relative BTCs; (b) cumulative BTCs.

to larger volumes of water added, clearly indicating retarded leaching of picloram. The decrease in the maximum concentrations of picloram in leachates was significant for all clay complexes (from 26 µM to 13–17 µM depending on the type of complex). In agreement with the batch release results, for the PM preparations the maximum

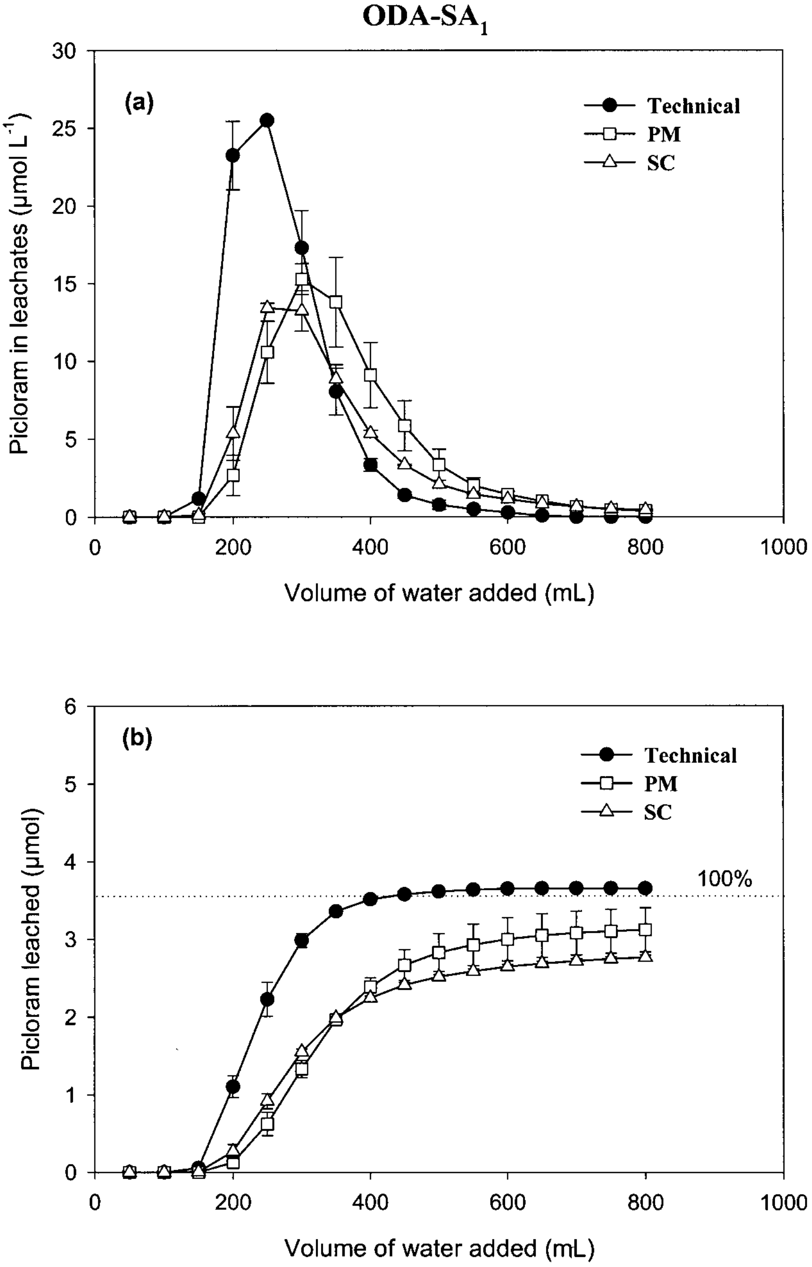

FIGURE 5 Picloram BTCs after application to soil columns as free technical product and ODA-SA_1 complexes: (a) relative BTCs, (b) cumulative BTCs.

concentrations of picloram in the leachates (17 µM for Fe-SW, 15 µM for ODA-SA_1 and 13 µM for HDTMA-SA_2) were inversely related to the affinities of the clays for picloram, while the total amounts of herbicide leached were close to 100% (Figs. 4, 5 and 6). For the SC preparations, the total amounts of picloram leached were in general

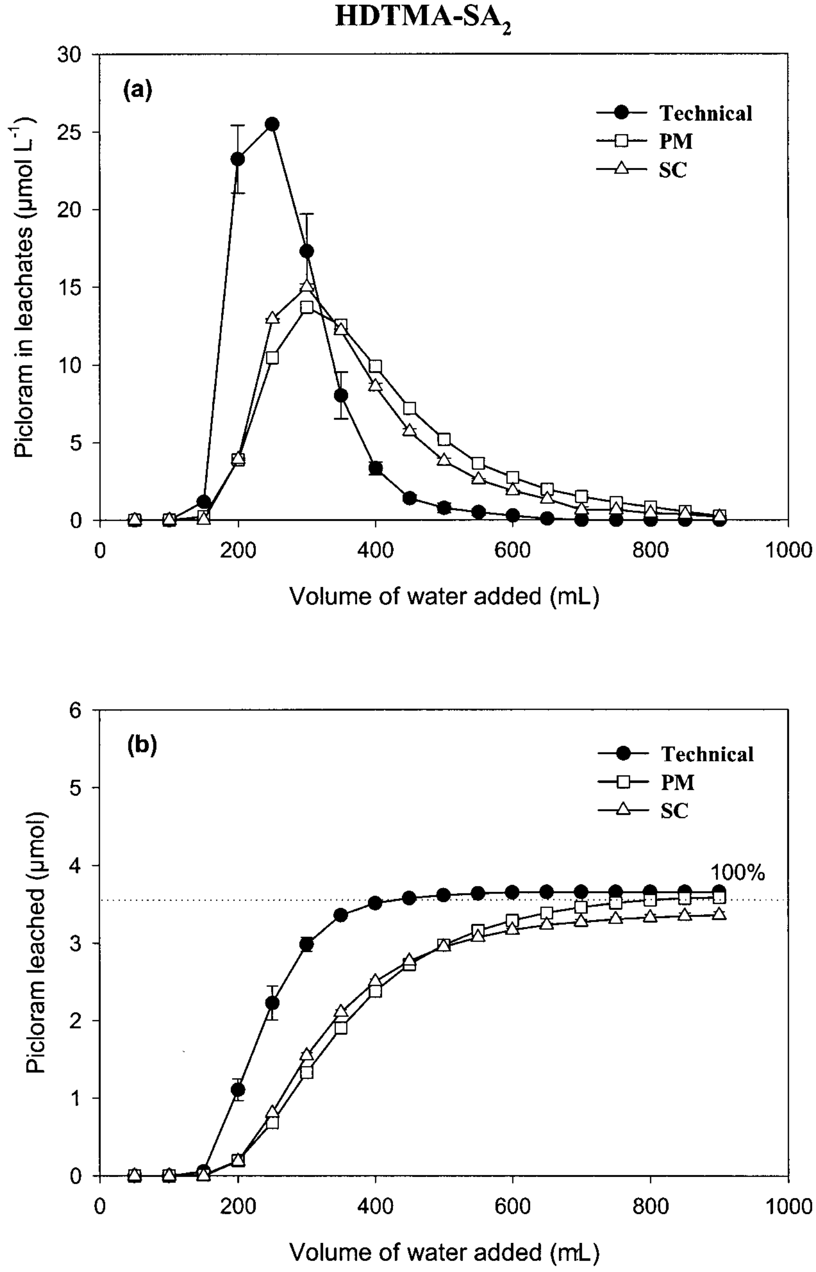

FIGURE 6 Picloram BTCs after application to soil columns as free technical product and HDTMA-SA$_2$ complexes: (a) relative BTCs; (b) cumulative BTCs.

lower compared to the PM preparations, in particular for Fe-SW and ODA-SA$_1$ where 25% of the herbicide applied did not leach from the soil column. As supported by the desorption and FT-IR spectroscopy results, it is likely that the amount of picloram not leached from the SC preparations of Fe-SW and ODA-SA$_1$ corresponded to some strong or irreversible sorption of the herbicide on the clay particles, which could have been favored by the addition of the organic solvent during the preparation of these complexes [8].

CONCLUSIONS

Replacement of the original inorganic cations of SWy-2 and SAz-1 montmorillonites with Fe^{3+} and alkylammonium cations resulted in clays with sorptive properties for the herbicide picloram. Clay–picloram complexes prepared from three clays with different affinities for the herbicide (Fe-SW, ODA-SA_1 and HDTMA-SA_2) displayed slow release properties in water and retarded picloram leching through soil columns compared with the application of the free technical compound. The total amounts of herbicide released from the complexes were in general close 100%, although some irreversible sorption occurred in intimate associations (SC) containing Fe^{3+} and ODA as exchange cations in the clays. In summary, our results showed that clay–herbicide complexes prepared from selectively-modified clays may be useful in reducing rapid leaching of highly mobile pesticides such as picloram.

Acknowledgments

This work has been partially supported by the MCYT projects AMB96-0445C02-01 and REN2001-1700-CO2-01/TECNO and by Research Group RNM-124 of Junta de Andalucía.

References

[1] M.C. Hermosín and J. Cornejo, *J. Environ. Qual.*, **22**, 325–331 (1993).
[2] R. Celis, L. Cox, M.C. Hermosín and J. Cornejo, *Environ. Sci. Technol.*, **33**, 1200–1206 (1999).
[3] R.M. Johnson and A.B. Pepperman, *Pestic. Sci.*, **53**, 233–240 (1998).
[4] T.J. Gish, M.J. Schoppet, C.S. Helling, A. Shirmohammadi, M.M. Schnecher and R.E. Wing, *Trans. ASAE*, **34**, 1738–1744 (1991).
[5] Z. Gerstl, A. Nasser and U. Mingelgrin, *J. Agric. Food Chem.*, **46**, 3797–3802 (1998).
[6] E. González-Pradas, M. Fernández-Pérez, M. Villafranca-Sánchez, F. Martínez-López and F. Flores-Céspedez, *Pestic. Sci.*, **55**, 546–552 (1999).
[7] Y. El-Nahhal, S. Nir, C. Serban, O. Rabinovitch and B. Rubin, *J. Agric. Food Chem.*, **48**, 4791–4801 (2000).
[8] M.C. Hermosín, M.J. Calderón, J.P. Aguer and J. Cornejo, *Pest Manag. Sci.*, **57**, 803–809 (2001).
[9] L. Cox, R. Celis, M.C. Hermosín and J. Cornejo, *J. Agric. Food Chem.*, **48**, 93–99 (2000).
[10] M.J. Carrizosa, M.J. Calderón, M.C. Hermosín and J. Cornejo, *Sci. Total Environ.*, **247**, 285–293 (2000).
[11] T. Undabeytia, S. Nir and B. Rubin, *J. Agric. Food Chem.*, **48**, 2767–2773 (2000).
[12] A. Nennemann, Y. Mishael, S. Nir, B. Rubin, T. Polubesova, F. Bergaya, H. Van Damme and G. Lagaly, *Appl. Clay Sci.*, **18**, 265–275 (2000).
[13] R.D. Zhang, A.J. Krzyszowska-Waitkus, G.F. Vance and J.G. Qi, *Adv. Environ. Res.*, **4**, 59–68 (2000).
[14] U.S. Environmental Protection Agency. *Prevention, Pesticides and Toxic Substances* (7508 W, EPA-738-F-95-018, 1995) pp. 1–11.
[15] J.S. Arnold and W.J. Farmer, *Weed Sci.*, **27**, 257–262 (1979).
[16] R.A. Kohl, C.G. Carlson and S.G. Wangemann, *Appl. Engineer. Agric.*, **10**, 497–503 (1994).
[17] R. Grover, *Weed Sci.*, **19**, 417–418 (1971).
[18] T. DeLuca, J. Larson, L. Thorma and G. Algard. *A Survey of Pesticide Residues in Groundwater in Montana*, (Montana Dep. Agric., U.S.A., 1989) Environ. Manag. Div. Tech. Rep. 89–1, Helena.
[19] U.S. Environmental Protection Agency, *Prevention, Pesticides and Toxic Substances* (7508 W, EPA-738-R95-019,1995) pp. 1–301. [www http://www.epa.gov/REDs/0096.pdf]

[20] J.A. Wood and D.H.J. Anthony, *J. Environ. Qual.*, **26**, 1308–1318 (1997).

[21] L.P. Pang, M.E. Close, J.P.C. Watt and K.W. Vicent, *J. Contaminant Hydrol.*, **44**, 19–46 (2000).

[22] G.A. O'Connor, P.J. Wierenga, H.H. Cheng and K.G. Doxtader, *Soil Sci.*, **130**, 157–162 (1980).

[23] E. Barriuso, D.A. Laird, W.C. Koskinen and R.H. Dowdy, *Soil Sci. Soc. Am. J.*, **58**, 1632–1638 (1994).

[24] C.R. Worthing and R.J. Hance. *The Pesticide Manual* (BCPC, Surrey, U.K., 1991), 9th Ed., 1141 pp.

[25] C.H. Giles, S.N. McEwan, S.N. Nakhwa and D. Smith, *J. Chem. Soc.*, **3**, 3973–3993 (1960).

[26] M.J. Carrizosa, W.C. Koskinen, M.C. Hermosín and J. Cornejo, *Appl. Clay Sci.*, **18**, 223–231 (2001).

[27] R. Haque and R. Sexton, *J. Colloid Interface Sci.*, **27**, 818–827 (1968).

[28] R. Celis, W.C. Koskinen, A.M. Cecchi, G.A. Bresnahan, M.J. Carrizosa, M.A. Ulibarri, I. Pavlovic and M.C. Hermosín, *J. Environ. Sci. Health*, **B34**, 929–941 (1999).

[29] R. Celis, L. Cox, M.C. Hermosín and J. Cornejo, *Intern, J. Environ. Anal. Chem.*, **65**, 245–260 (1996).

[30] W.F. Jaynes and S.A. Boyd, *Soil Sci. Soc. Am. J.*, **55**, 43–48 (1991).

[31] J.M. Brixie and S.A. Boyd, *J. Environ. Qual.*, **23**, 1283–1290 (1994).

[32] M.C. Hermosín and J. Cornejo, *Chemosphere*, **24**, 1493–1503 (1992).

[33] R. Celis, W.C. Koskinen, M.C. Hemosín, M.A. Ulibarri and J. Cornejo, *Soil Sci. Soc. Am. J.*, **64**, 36–43 (2000).

[34] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, 3rd Ed., 433pp. Chapman and Hall, London (1975).

[35] P.L. Ritger and N.A. Peppas, *J. Controlled Release*, **5**, 34–42 (1987).

[36] J.D. Fryer, P.D. Smith and J.W. Ludwig, *J. Environ. Qual.*, **8**, 83–86 (1979).