Inorganic and Organic Clays as Carriers for Controlled Release of the Herbicide Hexazinone

RAFAEL CELIS,* M. CARMEN HERMOSÍN, M. JOSÉ CARRIZOSA, AND
JUAN CORNEJO

Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, Avenida Reina Mercedes 10,
Apartado 1052, 41080 Sevilla, Spain

The risk of ground water contamination resulting from rapid leaching of highly soluble pesticides can be minimized through the application of the pesticide adsorbed on a matrix or carrier, which limits the amount of pesticide immediately available for undesirable losses. The use of natural materials for this purpose is of special interest in terms of economy and sustainability. In this work the adsorption of the herbicide hexazinone by two montmorillonites saturated with various inorganic and organic cations was determined and the ability of the two clays displaying the highest adsorption capacities [Fe^{3+}-saturated Wyoming montmorillonite, (Fe-SW) and hexadecyltrimethylammonium-saturated Arizona montmorillonite (HDTMA-SA)] to act as carriers for slow release of hexazinone and to reduce herbicide leaching losses was evaluated. Hexazinone formulations based on Fe-SW and HDTMA-SA displayed slow release properties in water and soil/water suspensions, reduced herbicide leaching in soil columns, and maintained herbicidal activity, as compared with the currently available commercial hexazinone formulation (wettable powder). Loosely bound hexazinone−HDTMASA formulations, which led to the slowest breakthrough of hexazinone in soil columns along with the greatest amounts of herbicide released from the clay particles, displayed the most interesting characteristics for their use as slow release formulations and to prevent ground water contamination.

KEYWORDS: Adsorption; herbicide; hexazinone; leaching; organoclays; slow release

INTRODUCTION

Environmental problems associated with pesticide use, particularly the use of highly mobile pesticides, are a current concern because of the increasing presence of these agrochemicals in ground and surface waters. To compensate for transport and degradation losses and to ensure adequate pest control for a suitable period, pesticides are applied at concentrations greatly exceeding those required for control of the target organisms, thus increasing the likelihood of runoff and leaching and hence the risk of surface and ground water contamination (*1, 2*). This problem is exacerbated in the case of highly soluble pesticides because the risk of offsite movement from the intended target area increases as the pesticide is quickly dissolved in the soil solution (*3*).

Most herbicide 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 (*4*). For highly soluble pesticides, these formulations may result in great pesticide losses shortly after application, before molecules have time to diffuse into soil aggregates and reach adsorption sites in soil colloids (*5*). Recently, increased attention has been directed to reduce pesticide transport losses by the development of less hazardous formulations, such as controlled-release (CR)

formulations, in which only a part of the active ingredient is in an immediately available form; the bulk of the herbicide is trapped or sorbed in an inert support and is gradually released over time (*4, 6*). Beneficial effects related to the use of CR formulations include reduction in the amount of chemical required for pest control, decrease in the risk of environmental pollution, savings in manpower and energy by reducing the number of applications required in comparison to conventional formulations, increased safety for the pesticide applicator, and a general decrease in nontarget effects (*2*).

Among the various materials proposed as pesticide carriers in CR formulations, recently there has been a renewed interest in the use of natural soil constituents, such as clays, iron oxides, or humic acids (*1, 4, 7−9*). Clays have unique properties, such as their high specific surface areas associated with their small particle size, low cost, and ubiquitous occurrence in most soil and sediment environments. In addition, the possibility exists to selectively modify clay mineral surfaces, for instance, through the incorporation of large organic cations in the interlayers, to improve their adsorption capacity for selected pesticides, and to control the desorption rate once added to the environment (*9−15*).

In this work, we have investigated the potential use of clays, unaltered and modified by the incorporation of alkylammonium cations in the interlayers, as carriers for CR of the herbicide hexazinone (**Figure 1**), which has a very high leaching potential

* Corresponding author (telephone +34 954624711; fax +34 954624002; e-mail rcelis@irnase.csic.es).
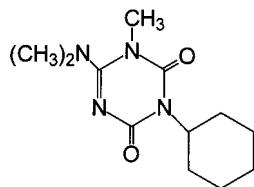
Clay Carriers of Hexazinone

J. Agric. Food Chem., Vol. 50, No. 8, 2002 **2325**

Figure 1. Chemical structure of hexazinone.

due to its high water solubility (33 g kg^{-1}), low adsorption by soil components, and relatively long persistence in soil (*16–18*). First, we determined hexazinone adsorption by two montmorillonites saturated with different inorganic and organic cations and selected two clays displaying high adsorption capacities for hexazinone: Fe^{3+}-saturated Wyoming montmorillonite (Fe-SW) and hexadecyltrimethylammonium-saturated Arizona montmorillonite (HDTMA-SA). Then, hexazinone formulations based on Fe-SW and HDTMA-SA were prepared and tested to slow the release of hexazinone to water and soil/water suspensions and to reduce herbicide leaching through soil, compared with the currently available commercial hexazinone formulation. Bioassays were also carried out to determine the herbicidal activity of the clay-based formulations prepared.

MATERIALS AND METHODS

Materials. The clays used in this study were Wyoming montmorillonite (SWy-2) and Arizona montmorillonite (SAz-1), purchased from the Source Clays Repository (Clay Minerals Society, Columbia, MO). The main difference between SWy-2 and SAz-1 is the density of layer charge in the octahedral layer, resulting in cation-exchange capacities (CEC) of 76 cmol$_c$ kg^{-1} for SWy-2 and 120 cmol$_c$ kg^{-1} for SAz-1. The original clays (SWy-2 and SAz-1) were saturated with Na$^+$, K$^+$, Mg^{2+}, and Fe^{3+} by treating 10 g of clay with 100 mL of a 1 M solution of NaCl, KCl, MgCl$_2$, or FeCl$_3$, respectively. After treatment (24 h, three times), the resulting homoionic clays were washed with distilled water until Cl-free and then lyophilized.

Four different organic cations, octadecylammonium (ODA), octadecyldimethylammonium (DODDMA), phenyltrimethylammonium (PTMA), and hexadecyltrimethylammonium (HDTMA), were used for the synthesis of the organic clays. For the synthesis, 10 g of SWy-2 or SAz-1 was treated with 100 mL of an ethanol/water (50:50) solution containing an amount of alkylammonium (chloride salt) equal to the CEC of the clay. The suspensions were shaken for 24 h, centrifuged, washed with distilled water until Cl-free, and then lyophilized. Physicochemical characteristics of inorganic and organic clays are included in **Table 1**. The organic carbon (OC) content was determined using a Perkin-Elmer 240C elemental analyzer (Perkin-Elmer Corp., Norwalk, CT), whereas the basal spacing values (d_{001}) were obtained from the X-ray diffractograms of oriented specimens, recorded with a Siemens D-5000 diffractometer (Siemens, Stuttgart, Germany) using Cu Kα radiation.

Analytical grade hexazinone, purity = 99.5% (Dr. Ehrenstorfer Lab.), was used to prepare the external standards for hexazinone analysis and to prepare the initial herbicide solutions used in adsorption experiments. Commercial hexazinone (wettable powder, Velpar 90%, Du Pont Ibérica S.A.) was used to prepare the clay-based formulations of the herbicide and also as a reference standard formulation in the release, leaching, and herbicidal activity experiments. The soil used in these experiments was a sandy-clay soil classified as Typic Rhodoxeralf. Soil texture (20% clay, 10% silt, and 70% sand) was determined by sedimentation and clay mineralogy (12% illite, 4% montmorillonite, and 4% kaolinite) by X-ray diffraction on oriented specimens (*19*). Soil pH was 7.9 in a 1:2 (w/w) soil/deionized water mixture. The organic matter content (0.99%) was determined according to the Walkley–Black method (*19*).

Adsorption Study. Hexazinone adsorption isotherms on inorganic and organic clays were obtained by the batch equilibration technique using 50-mL polypropylene centrifuge tubes. Initial hexazinone (analytical grade, 99.5%) solutions were prepared in distilled water at

concentrations (C_{ini}) ranging from 50 to 1500 μM. Duplicate 20-mg adsorbent samples were equilibrated with 8 mL of hexazinone 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 supernatants by high-performance liquid chromatography (HPLC). The amount of herbicide adsorbed (C_s) was calculated from the difference between the initial (C_{ini}) and the equilibrium (C_e) solution concentrations. Adsorption isotherms were fit to the logarithmic form of the Freundlich equation: log C_s = log K_f + 1/n_f log C_e, where C_s (mmol kg^{-1}) is the amount of herbicide adsorbed at the equilibrium concentration C_e (mmol L^{-1}) and K_f and 1/n_f are the empirical Freundlich constants.

Preparation of Clay-Based Formulations of Hexazinone. Three types of formulations with increasing degrees of clay–herbicide association were prepared with two selected adsorbents (Fe-SW and HDTMA-SA): (i) a physical mixture (PM) was obtained by thoroughly mixing 44 mg of commercial hexazinone with 956 mg of clay or organoclay without solvent addition; (ii) a weak association complex (WC) was prepared by adding 2 mL of methanol to 1 g of PM, which was then allowed to dry; (iii) a strong association complex (SC) was prepared by adding 10 mL of methanol to 1 g of PM, followed by 24 h of shaking and then air-drying. The amount of hexazinone in all formulations corresponded to a 4% content in active ingredient (ai). 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 WC and SC formulations favors the clay–herbicide interaction, making the release of the herbicide from these formulations slower compared to that of the PM (*9*). Therefore, a range of release rates of hexazinone was expected for the three types of formulations prepared.

Batch Release Study. The release of hexazinone from the commercial formulation and the clay complexes was monitored in water and soil/water suspensions. One milligram of hexazinone (ai) was added to distilled water (250 mL) or to a soil/water suspension (250 g/250 mL) in glass bottles lined with screw caps. At selected times after herbicide application (from 0 to 196 h), the bottles were hand-shaken, the contents were allowed to settle for 10 min, and then 2 mL of the supernatant solution was filtered and the hexazinone concentration was determined by HPLC. The periodical removal of such a small amount of supernatant was assumed not to have any influence on the release pattern. In all cases, hexazinone release kinetics was obtained in duplicate.

Column Leaching Study. Leaching was studied in 30 × 5 cm methacrylate columns made up of six 5-cm-long sections sealed with silicon. The top ring was filled with sea sand and the bottom ring with sea sand plus glass wool, to minimize losses of soil and contamination of leachates with soil particles. The other four rings were hand-packed with 490 g of air-dried soil, saturated with 300 mL of 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 hexazinone corresponding to an application rate of 10 kg of ai ha^{-1} (1.96 mg of ai) was applied to the top of duplicate soil columns as commercial formulation or as clay complexes suspended in 25 mL of 0.01 M CaCl$_2$. The columns were leached with 0.01 M CaCl$_2$ at a rate of 25 mL day^{-1} until no herbicide was detected in the leachates. This was achieved within a 60-day period. At the end of the leaching experiment, soil samples from the different rings (0–5-, 5–10-, 10–15-, and 15–20-cm depths) were extracted once with 100 mL of a 1:1 methanol/water mixture by shaking mechanically at 20 ± 2 °C for 24 h. The suspensions were centrifuged, filtered, and analyzed by HPLC in order to determine the residual amount of hexazinone at the different depths of the soil column. Preliminary experiments showed that this extraction procedure recovered >95% of the herbicide freshly applied to the soil.

Bioassay. The herbicidal activity of the different hexazinone formulations was studied using garden watercress (*Lepidium sativum*) seeds. Eight-centimeter diameter pots were filled with 220 g of soil, saturated with water, and allowed to drain for 24 h. Fifteen seeds of garden watercress (Royalfleur) were gently distributed on the surface of each pot and incubated in a growth chamber. The pots were watered daily with 10 mL of distilled water, and 1 week after sowing, the commercial or clay-based formulations of hexazinone were applied

Table 1. Characteristics of Inorganic and Organic Clays and Freundlich Coefficients, K_f and $1/n_f$, for Hexazinone Adsorption[a]

organoclay	montmorillonite	interlayer cation	OC (%)	OCtS (%)	d_{001} (nm)	K_f	$1/n_f$
K-SW	SWy-2	K^+			1.1	16 (14–18)	0.82 (±0.06)
Na-SW	SWy-2	Na^+			1.3	24.5 (24–25)	0.79 (±0.01)
Mg-SW	SWy-2	Mg^{2+}			1.5	28 (23–34)	0.85 (±0.09)
Fe-SW	SWy-2	Fe^{3+}			1.2	468 (298–735)	0.88 (±0.15)
ODA-SW	SWy-2	ODA	14.8	90	1.7	37 (33–41)	0.59 (±0.06)
DODDMA-SW	SWy-2	DODDMA	31.3	90	3.3	40 (36–44)	0.88 (±0.05)
PTMA-SW	SWy-2	PTMA	6.8	83	1.5	88 (81–95)	0.44 (±0.03)
HDTMA-SW	SWy-2	HDTMA	14.7	85	1.8	29 (27–31)	0.76 (±0.06)
ODA-SA	SAz-1	ODA	25.5	98	3.7	51 (38–68)	0.72 (±0.06)
DODDMA-SA	SAz-1	DODDMA	38.3	70	4.0	25 (21–29)	0.71 (±0.09)
PTMA-SA	SAz-1	PTMA	9.7	75	1.5	9 (8–10)	1.13 (±0.10)
HDTMA-SA	SAz-1	HDTMA	22.8	85	2.4	184 (159–212)	0.92 (±0.07)

[a] OCtS, percentage of the CEC of the clay saturated with organic cation (calculated from the organic C content); d_{001}, basal spacing; K_f, $1/n_f$: Freundlich coefficients for hexazinone adsorption (values in parentheses are standard error ranges about the mean).
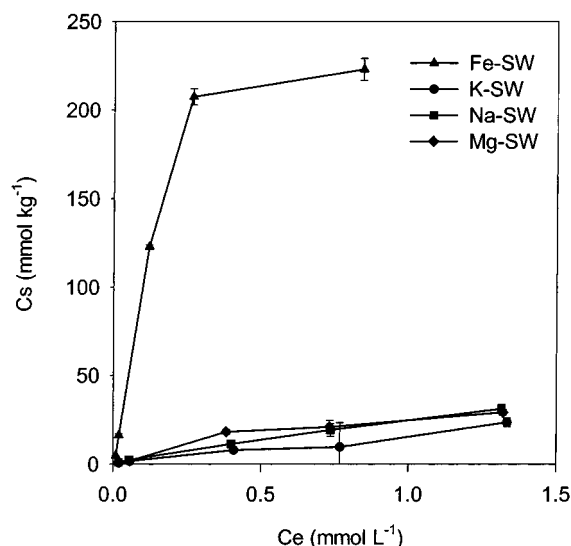
Figure 2. Hexazinone adsorption isotherms on SW montmorillonite saturated with different inorganic cations.

postemergence at an application rate of 10 kg of ai ha^{-1}. This application rate is within the range of 6–12 kg ha^{-1} recommended for field application of hexazinone (20). Herbicidal efficacy was determined 1 week after herbicide application by visual evaluation of the weed control efficacy.

Herbicide Analysis. Hexazinone analysis was performed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode array detector. The following conditions were used: 70:30 water/acetonitrile eluent mixture at a flow rate of 1 mL min^{-1}, Novapak C18 column (150 mm length × 3.9 mm i.d.), 25 μL injection volume, and UV detection at 247 nm. External calibration curves with standard solutions between 1 and 1500 μM were used in the calculations.

RESULTS AND DISCUSSION

Hexazinone Adsorption by Inorganic and Organic Clays. Hexazinone adsorption isotherms on SW and SA montmorillonites saturated with different inorganic cations showed very high adsorption on Fe-SW, low adsorption on Mg-SW, Na-SW, and K-SW, and negligible adsorption on SA montmorillonite (**Figure 2**). The high adsorption of hexazinone observed on Fe-SW compared to Mg-, Na-, and K-SW (**Figure 2**) has previously been reported for other weakly basic pesticides and attributed to protonation of the pesticide in the interlayers of the Fe-saturated clay mineral followed by retention by a cationic exchange mechanism, as a result of the high surface acidity induced by the interlayer Fe^{3+} ions (21–24). The lack of adsorption observed on SA montmorillonite (not shown) is

attributed to the high surface charge density of this clay, resulting in very little hydrophobic, noncharged surface available for the adsorption of neutral pesticide molecules (23, 25, 26).

Except for PTMA-SW and HDTMA-SA, replacement of the original inorganic cation with alkylammonium cations did not greatly increase the adsorption capacity of the clays for hexazinone (**Figure 3**; **Table 1**). These results are in contrast to previous work reporting a great improvement of the adsorption capacity of clays for hydrophobic molecules after incorporation of organic cations in the clay mineral interlayers (11, 27, 28). The high polarity of the herbicide hexazinone (water solubility = 33 g kg^{-1}) may have limited its affinity for the organic phase of the organoclays, thus explaining the relatively low adsorption measured. In fact, it appears that the presence of unoccupied interlayer space, available for pesticide adsorption, more than other organoclay properties such as the organic C content or the basal spacing value, have governed the uptake of hexazinone by the organic clays. This is supported by the large adsorption measured on PTMA-SW and HDTMA-SA compared to organoclays with a more compact packing of the organic phase (**Figure 3**; **Table 1**). In the case of PTMA-SW, the low surface charge density of SW combined with the small size of the PTMA cation resulted in considerable interlayer surface not covered by the organic cation and hence available for herbicide adsorption (29, 30). Such a surface has been suggested to have hydrophobic properties bestowed on it by the organic cations and by the areas of exposed silicate oxygens (29–31). These characteristics allow hexazinone molecules to effectively compete with water molecules for adsorption sites on the siloxane surface. Similarly, for HDTMA-SA, the voluminous trimethylammonium group together with the vertical arrangement of the hexadecyl chains ($d_{001} > 2.2$ nm) (32) also results in considerable space between two adjacent organic cations, available to host herbicide molecules (33). In agreement with results recently reported by Aguer et al. (33) for the highly polar herbicide fenuron (water solubility = 3.85 g kg^{-1}), our results indicate that the presence of free spaces in the interlayers, available to host the herbicide, is a major factor controlling the adsorption of hexazinone by organoclays.

Clay-Based Formulations of Hexazinone. On the basis of the adsorption results, the two most adsorptive clays, Fe-SW and HDTMA-SA, were selected as carriers in the preparation of controlled-release formulations of hexazinone. For each clay, three clay–herbicide complexes (4% ai) were prepared: a physical mixture (PM), a weak association complex (WC), and a strong association complex (SC). As mentioned above, previous work has shown that the organic solvent used in the preparation of WC and SC formulations favors the clay–
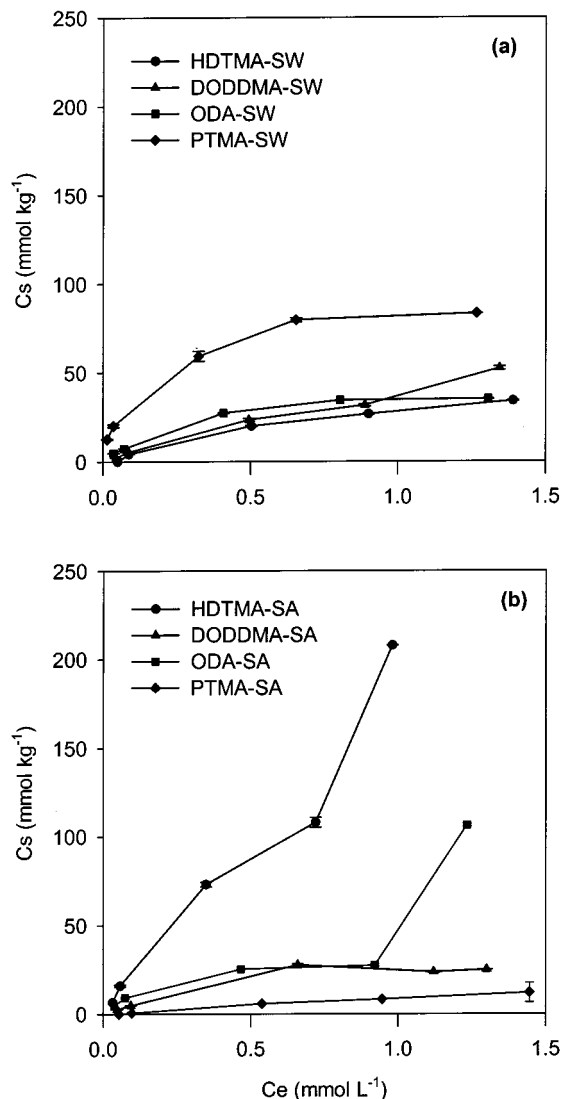
Clay Carriers of Hexazinone

J. Agric. Food Chem., Vol. 50, No. 8, 2002 **2327**

Figure 3. Hexazinone adsorption isotherms on organoclays: (a) SW-organoclays; (b) SA-organoclays.
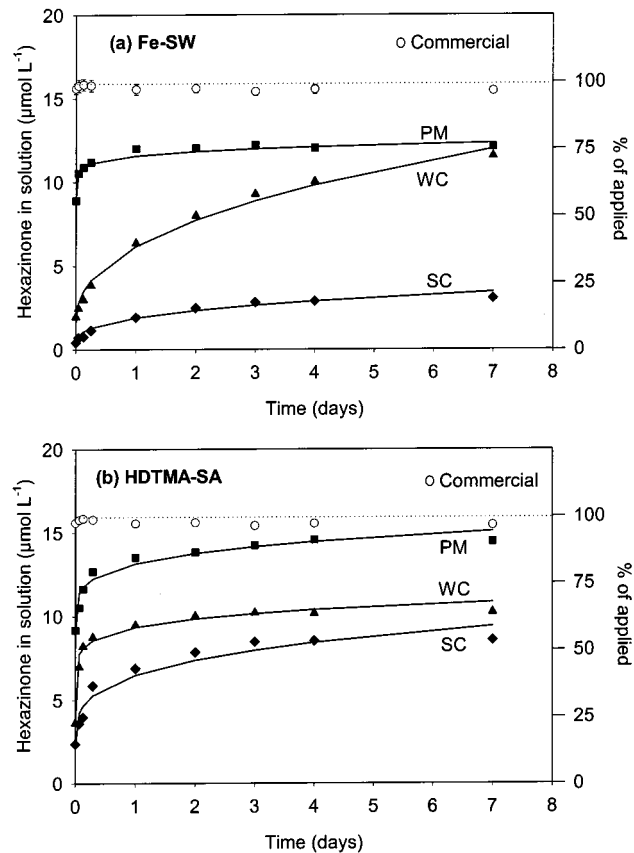

Figure 4. Hexazinone release kinetics in water from commercial and clay-based formulations: (a) Fe-SW formulations; (b) HDTMA-SA formulations. Symbols are experimental data points, whereas lines are fittings to the equation $M_t/M_z = kt^n + c$.

herbicide interaction, making the release of the herbicide from these formulations slower compared to that by the PM (*9*). Hermosín et al. (*9*) found that association of the herbicide fenuron with montmorillonite in SC formulations was even stronger compared to WC, most likely because the higher amount of methanol used and the longer time required for drying facilitated the diffusion of the herbicide within the clay aggregates, thus favoring retention and/or trapping of the herbicide during methanol evaporation. On the basis of these results, we expected a range of release rates of hexazinone for the three types of formulations prepared.

Release Study. The release of hexazinone from the several Fe-SW and HDTMA-SA formulations in water and water/soil suspension is shown in **Figures 4** and **5**. In contrast to the commercial formulation, with 100% instantaneous release, all clay-based formulations of hexazinone displayed slow-release properties in water, with decreasing herbicide release in the order PM > WC > SC (**Figure 4**). The Fe-SW complexes displayed an initial release (*t* = 0) from 5 to 55% of the herbicide and a final release (*t* = 7 days) from 15 to 75%, depending on the type of preparation. For HDTMA-SA complexes, the initial release was from 15 to 60% and the final release from 50 to 90% (**Figure 4**). It should be noted that the amount of hexazinone retained at the end of the experiment was significant

for some of the formulations assayed: 40 and 50% for WC and SC of HDTMA-SA, respectively, and 85% for SC of Fe-SW. It is likely that this represents herbicide irreversibly bound or entrapped within the clay aggregates as a result of the wetting−drying cycle carried out during the preparation of the WC and SC formulations (*34*).

Hexazinone release data in water were analyzed by applying the generalized model (*6, 35*)

$$M_t/M_z = kt^n + c$$

where M_t/M_z is the percentage of pesticide released at time *t* and *k*, *n*, and *c* are constants that are characteristic of the systems. These parameters are given in **Table 2** for all clay−hexazinone formulations, together with t_{50} values (time taken for 50% of ai to be released) calculated using the corresponding equation. The decrease in *c* values in the order PM > WC > SC indicates a decrease in the initial release (*t* = 0), whereas the increase in t_{50} values from PM to SC indicates a decrease in the release rate (*6*). Thus, a range of rates and extents of hexazinone release occurred depending on the adsorbent (Fe-SW or HDTMA-SA) and the type of preparation (PM, WC, or SC), suggesting the possibility to select diverse preparations according to the intended use.

In soil/water suspensions the release profiles of hexazinone showed characteristics similar to those obtained in water, with decreasing herbicide release, for both Fe-SW and HDTMA-SA formulations, in the following order: commercial ≥ PM > WC > SC (**Figure 5**). In the presence of soil, the final release of hexazinone applied as commercial formulation was <100%,
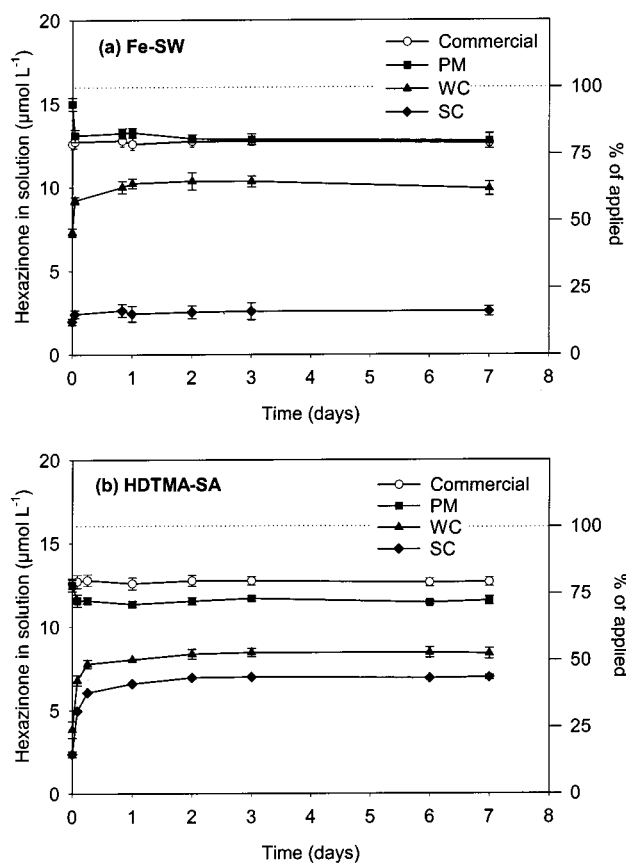
Figure 5. Hexazinone release kinetics in soil/water suspensions from the commercial and clay-based formulations: (a) Fe-SW formulations; (b) HDTMA-SA formulations.

Table 2. Constants from Fitting the Equation $M_t/M_z = kt^n + c$ to the Release Data of Hexazinone in Water for Clay-Based Formulations

formulation	k	n	c	r	t_{50} (days)
Fe-SW (PM)	17 ± 2^a	0.13 ± 0.02	56 ± 1	0.98	<0.01
Fe-SW (WC)	29 ± 3	0.42 ± 0.05	10 ± 2	0.99	2.2
Fe-SW (SC)	10 ± 2	0.35 ± 0.07	2 ± 1	0.98	88
HDTMA-SA (PM)	26 ± 4	0.20 ± 0.04	57 ± 3	0.97	<0.01
HDTMA-SA (WC)	36 ± 3	0.12 ± 0.02	23 ± 3	0.99	0.1
HDTMA-SA (SC)	28 ± 5	0.26 ± 0.06	13 ± 4	0.97	2.9

^{a} Value ± standard error.

which is due to some herbicide adsorption by the soil particles. Accordingly, the final amounts of hexazinone released into solution from PM, WC, and SC formulations were also slightly lower than the amounts released in water. An interesting feature of **Figure 5** is that the release of hexazinone from the different formulations was in general faster than that observed in water (**Figure 4**). The presence of soil particles in the soil/water experiment appears to result in a more effective shaking of the clay particles, reducing the equilibrium time for herbicide release.

Leaching Study. The location of the maximum concentration peak, close to 1 pore volume ($V_o = 200$ mL), in the commercial hexazinone breakthrough curve (BTC) indicates little retention of the herbicide in the soil column (**Figures 6** and **7**). The application of the herbicide as Fe-SW and HDTMA-SA complexes clearly resulted in lower hexazinone concentration in leachates, flattening of the BTC, and, in the case of HDTMA-SA formulations, shifting of the maximum concentration peak to larger water volumes compared to the commercial formulation (**Figures 6a** and **7a**). For both Fe-SW and HDTMA-SA
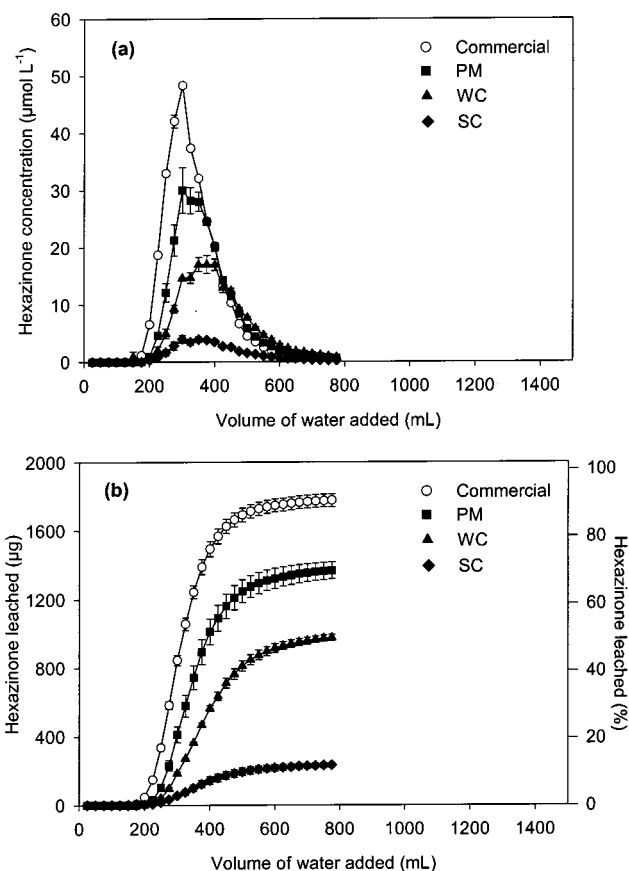

Figure 6. Hexazinone BTCs after application to soil columns as commercial and Fe-SW formulations: (a) relative BTCs; (b) cumulative BTCs.

formulations, hexazinone concentrations in leachates decreased in the order commercial > PM > WC > SC, which is in accordance with the release rates observed in the batch release study. Thus, leaching data indicate that hexazinone applied as clay-based formulations leached less than the commercial formulation and that the possibility exists to select the type of formulation to render different leaching patterns according to the desired behavior. It should be noted that, taking into account the time scale of **Figures 6** and **7** (25 mL day^{-1}), the release of hexazinone was much slower under column leaching than in batch soil/water suspension. This is because the surface contact between the clay particles and water at the surface of the soil column is less effective than that in the static batch system.

Cumulative BTCs (**Figures 6b** and **7b**) showed total amounts of hexazinone leached that were in agreement with the final releases observed in the batch study (**Figure 4**). Because negligible amounts of hexazinone remained in the soil columns at the end of the leaching experiment (data not shown), the amounts of hexazinone not leached should correspond to the sum of herbicide degraded, irreversibly bound to soil, and irreversibly bound (or entrapped) to the clay particles in the formulation. The fact that 90% of hexazinone applied as commercial formulation was recovered in leachates suggests that the extent of degradation and irreversible adsorption to soil was small (i.e., 10%), and hence most of the herbicide not leached from the different formulations should correspond to herbicide entrapped or irreversibly bound to Fe-SW and HDTMA-SA clay particles.

Although the decrease in hexazinone concentration in leachates was significant for both Fe-SW and HDTMA-SA complexes, flattening of the BTC and retardation of the herbicide in the
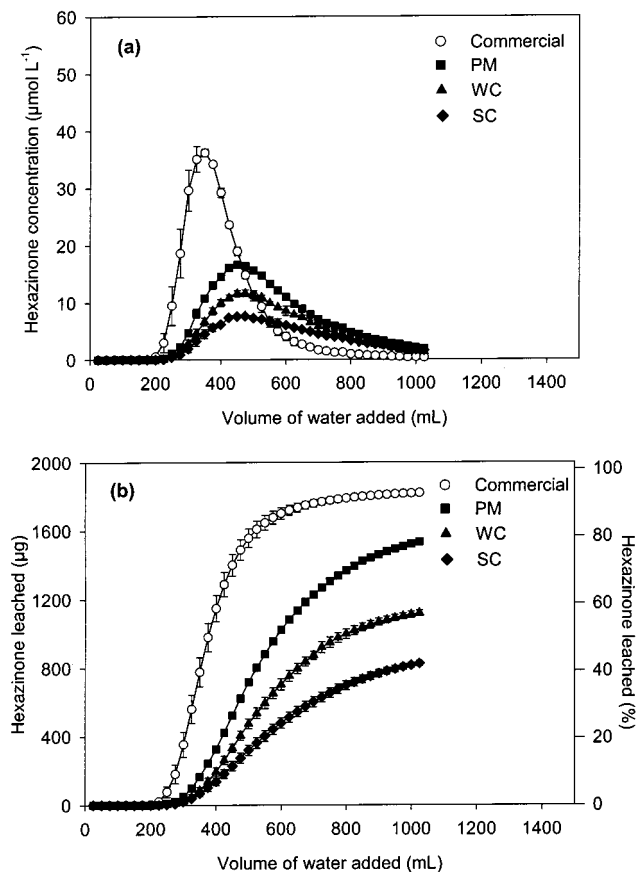
Clay Carriers of Hexazinone

J. Agric. Food Chem., Vol. 50, No. 8, 2002 **2329**

Figure 7. Hexazinone BTCs after application to soil columns as commercial and HDTMA-SA formulations: (a) relative BTCs; (b) cumulative BTCs.

soil column were more evident for HDTMA-SA (**Figure 7**). The maximum concentration of hexazinone occurred in the leachates of PM, WC, and SC 4 days (100 mL) later compared to the commercial formulation, thus extending the presence of hexazinone in leachates at moderate concentrations up to 1000 mL of water added (**Figure 7a**). This is, in fact, one of the most desirable features of controlled-release formulations, because the decrease in herbicide concentration in leachates without shifting of the maximum concentration peak can be an artifact due to the amount of herbicide molecules that are irreversibly adsorbed to the clay particles and, therefore, not available for leaching. In this regard, the loosely bound formulations, such as PM and WC, of HDTMA-SA organoclay, showing the greatest retardation along with the lowest amounts of hexazinone not released, display the most interesting characteristics for their use as slow-release formulations of hexazinone. The strong association complexes (SC), displaying final release of hexazinone of <60%, may not be environmentally and economically interesting because the high amounts of hexazinone residues not released from the formulations would result in soil contamination and would require higher application rates for the same amount of active ingredient to be released.

Bioassay. The herbicidal activity of hexazinone was assessed for all formulations prepared (not shown). The results indicated that all clay-based formulations of hexazinone applied post-emergence were as effective as the commercial formulation in the control of garden watercress (*Lepidium sativum*). The application rate of hexazinone used in these experiments (10 kg ha^{-1}) was within the range of 6–12 kg ha^{-1} recommended for field application of the herbicide (*20*). These results confirm that clay-based formulations can be used at application rates within those recommended for soil application of hexazinone, reducing herbicide leaching through soil while maintaining weed control efficacy.

The results of this work show, in summary, that hexazinone formulations based on inorganic (Fe-SW) and organic (HDTMA-SA) clays display controlled-release properties in water and soil/water suspensions, reduce herbicide leaching in soil columns, and retain herbicidal activity as compared with the currently available commercial hexazinone formulation. A range of rates and extents of hexazinone release and leaching patterns occur depending on the adsorbent (Fe-SW or HDTMA-SA) and the preparation procedure (with or without organic solvent addition), suggesting the possibility to select diverse preparations according to the intended use. Among the different clay-based formulations assayed in this work, loosely bound hexazinone–organoclay formulations (such as the HDTMASA–hexazinone physical mixture) showed the greatest retardation along with the lowest amounts of herbicide irreversibly bound to the clay particles, thus displaying the most interesting characteristics for their use as slow-release formulations of hexazinone. These formulations, therefore, are suggested to minimize leaching losses of highly mobile herbicides, such as hexazinone, thus preventing loss of biological activity, on the one hand, and decreasing the risk of ground water contamination on the other.

ABBREVIATIONS USED

BTC, breakthrough curve; CEC, cation exchange capacity; CR, controlled release; DODDMA, dioctadecyldimethylammonium; HDTMA, hexadecyltrimethylammonium; OC, organic carbon; ODA, octadecylammonium; PM, physical mixture; PTMA, phenyltrimethylammonium; SA, Arizona montmorillonite; SC, strong association complex; SW: Wyoming montmorillonite; WC, weak association complex.

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2330 *J. Agric. Food Chem.,* Vol. 50, No. 8, 2002

Celis et al.

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