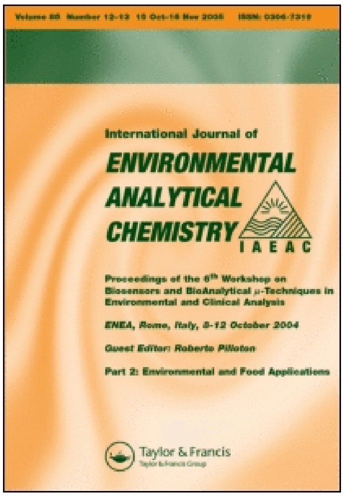

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Assessing factors influencing the release of hexazinone from clay-based formulations

Rafael Celis[a]; Gracia Facenda[a]; M. Carmen Hermosín[a]; Juan Cornejo[a]
[a] Instituto de Recursos Naturales y Agrobiología de Sevilla, 41080 Seville, Spain

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Assessing factors influencing the release of hexazinone from clay-based formulations

RAFAEL CELIS*, GRACIA FACENDA,
M. CARMEN HERMOSÍN and JUAN CORNEJO

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

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New designs of pesticide formulations based on organoclays are receiving increasing attention in reducing offsite movement of pesticides in the environment and in prolonging the efficacy of soil-applied pesticides. In the present article, we report the results of laboratory and field experiments conducted to evaluate the influence of the saturating cation, the sorbent : herbicide ratio, and the type of preparation on the controlled release properties of organoclay-based formulations of the herbicide hexazinone. Two organoclays with different affinities for hexazinone (hexadecyltrimethylammonium-exchanged Arizona montmorillonite, HDTMA-SA, and phenyltrimethylammonium-exchanged Arizona montmorillonite, PTMA-SA), two herbicide loadings (10% and 20% AI), and three types of preparation were assayed. Laboratory experiments showed that hexazinone formulations based on HDTMA-SA displayed slow-release properties in water, retarded herbicide leaching through soil columns, and maintained a herbicidal efficacy similar to that of the currently available commercial hexazinone formulation (wettable powder). In contrast, PTMA-SA formulations released the herbicide instantaneously and did not display slow-release properties. High organoclay-herbicide ratios and the use of organic solvent made the interaction between HDTMA-SA and the herbicide more intimate and reduced the release rate of hexazinone, suggesting that a range of release and leaching behaviours can be achieved by selecting the type of preparation and the herbicide loading in the formulations. A field experiment confirmed the usefulness of HDTMA-SA formulations of hexazinone to reduce herbicide leaching while maintaining weed-control efficacy.

Keywords: Adsorption; Herbicide; Hexazinone; Leaching; Organoclays; Slow release

1. Introduction

The presence of pesticide residues in ground and surface water has raised concerns for the protection of the environment, in particular the protection of drinking-water quality [1]. Pesticides with a high water solubility are particularly susceptible of runoff and leaching, because the risk of offsite movement from the intended target area greatly increases as the pesticide is quickly dissolved in the soil solution [2]. Since one major source of ground and surface water contamination results from pesticide application in an immediately

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*Corresponding author. Fax: +34-954624002. Email: rcelis@irnase.csic.es
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available form that is readily released to the environment [3], renewed attention is being directed to designing less hazardous, sustainable formulations, such as controlled-release (CR) formulations, which supply the active ingredient (AI) gradually over time, thereby decreasing the risk of offsite movement of highly mobile pesticides [4–13].

Clay minerals were suggested long ago as pesticide carriers in CR formulations due to their attractiveness in terms of economy and sustainability [1]. Currently, new designs of pesticide formulations on the basis of surface-modified clay minerals are being proposed to improve the affinity of clay minerals for selected pesticides and to control the desorption rate once added to the environment [3–6, 8, 9, 11, 12–17]. Incorporation of organic cations within the clay mineral interlayers, for instance, modifies the nature of the surface from hydrophilic to hydrophobic enhancing its affinity for organic pesticides. Considerable attention has been given to describe the diversity of organoclay–pesticide interactions [13–15, 18–25], which should be helpful for the development of pesticide formulations with the desired behaviour. However, there is only limited information on the factors influencing the release rate and extent of pesticides from organoclay formulations, such as the nature of the organic cation or the sorbent : pesticide ratio [5, 6, 8, 9, 11–17], and particularly scarce are studies that validate the behaviour of organoclay formulations of pesticides under real field conditions [5, 16, 17]. This information is essential to optimize the design of pesticide–organoclay formulations and their application for agricultural use.

In a previous article, we investigated the potential use of two montmorillonites saturated with several inorganic and organic cations as carriers for CR of the herbicide hexazinone, a herbicide with a very high leaching potential due to its high water solubility (33 g/kg), low adsorption by soil components, and relatively long persistence in soil [11]. Organoclays led to a slower breakthrough of the hexazinone in soil columns and higher amounts of herbicide released compared with clays saturated with inorganic cations, thus displaying more interesting characteristics as carriers for CR formulations. However, one major limitation of many of the formulations assayed was the high amount of hexazinone not released from the formulations, which would result in soil contamination and would require higher application rates for the same amount of active ingredient to be released. In the present paper, we investigated the effect of varying the interlayer organic cation, the sorbent : herbicide ratio, and the type of preparation on the release behaviour of hexazinone from organoclays. Two organic cations with different affinities for hexazinone (one adsorptive, phenyltrimethylammonium, and one organophilic, hexadecyltrimethylammonium), two herbicide loadings (10% and 20%), and three different types of preparation were tested. Experiments were also conducted with selected formulations to evaluate their ability to reduce hexazinone leaching through soil and to test their herbicidal efficacy in both laboratory and field conditions. The information provided should be valuable to optimize the characteristics of pesticide-organoclay formulations for practical applications.

2. Experimental

2.1. *Materials*

The clay used in this study was Arizona montmorillonite, SAz-1, purchased from the Source Clays Repository (Clay Minerals Society, Columbia, MO).

Table 1. Characteristics of the organoclays and Freundlich coefficients, K_f and $1/n_f$, for hexazinone adsorption[a].

Organoclay	Montmorillonite	Interlayer cation	OC (%)	OCtS (%)	d_{001} (nm)	K_f	$1/n_f$
PTMA-SA	SAz-1	PTMA	9.7	75	1.5	9 (8–10)	1.13 (1.03–1.23)
HDTMA-SA	SAz-1	HDTMA	22.8	85	2.4	184 (159–212)	0.92 (0.85–0.99)

[a] PTMA: phenyltrimethylammonium; HDTMA: hexadecyltrimethylammonium; OC: organic C content; 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).

Table 2. Physicochemical characteristics of the soils.

Soil	pH	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Fe_2O_3(%)
Typic Rhodoxeralf (laboratory study)	7.9	1.24	71	9	20	1.04
Typic Rhodoxeralf (field experiment)	7.6	0.90	64	19	17	–

Hexadecyltrimethylammonium- and phenyltrimethylammonium-exchanged montmorillonite (HDTMA-SA and PTMA-SA) were prepared by treating 10 g of SAz-1 with 100 mL of an ethanol + water (1 + 1 by volume) solution containing an amount of alkylammonium (chloride salt) equal to the cation exchange capacity of the clay (CEC = 120 $cmol_c$/kg). The suspensions were shaken for 24 h, centrifuged, washed with distilled water until Cl-free, and then lyophilized. The physicochemical characteristics of HDTMA-SA and PTMA-SA organoclays are given in table 1. The organic carbon (OC) content was determined using a Perkin Elmer 240C elemental analyser (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) using CuK_α radiation.

Analytical-grade hexazinone, purity 99.5%, (Dr. Ehrenstorfer Lab., Germany), was used to prepare the external standards for hexazinone analysis and the initial herbicide solutions used in adsorption experiments. Commercial hexazinone (wettable powder, Velpar 90%, Du Pont Ibérica S.A., Spain) was used to prepare the organoclay-based formulations of the herbicide and also as a reference standard formulation in the release, leaching, and herbicidal activity experiments.

The soil used in the laboratory experiments was a sandy clay soil from Coria del Río (Seville, Spain), classified as Typic Rhodoxeralf. The soil was sampled (0–20 cm), air-dried, sieved (2 mm), and stored at 4°C until used. The field experiment was conducted in a field plot from the same area (Coria del Río, Seville) and therefore with similar soil characteristics. The physicochemical characteristics of the soils are listed in table 2. Soil texture was determined by sedimentation [26], soil pH was measured in a soil + deionized water mixture (1 + 1 by weight), and the organic matter content was determined according to the Walkley–Black method [26].

2.2. *Adsorption experiment*

Hexazinone adsorption isotherms on HDTMA-SA and PTMA-SA 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 organoclay samples (20 mg) were equilibrated with hexazinone initial solutions (8 mL) by shaking mechanically at $20 \pm 2°\mathrm{C}$ for 24 h. After equilibration, the suspensions were centrifuged, and the equilibrium concentrations (C_e) were 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 fitted 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) is the amount of herbicide adsorbed at the equilibrium concentration C_e (mmol/L), and K_f and $1/n_f$ are the empirical Freundlich constants.

2.3. *Preparation of hexazinone–organoclay complexes*

Three types of herbicide–organoclay complexes were prepared with HDTMA-SA and PTMA-SA organoclays: (1) a physical mixture (PM) was obtained by thoroughly mixing the organoclay and the herbicide without solvent addition; (2) a weak-association complex (WC) was prepared by adding 2 mL of methanol to 1 g of PM, then allowing to dry; (3) a strong-association complex (SC) was prepared by adding 10 mL of methanol to 1 g of PM, shaking for 24 h, then air-drying. Formulations with two different herbicide loadings (10% and 20% AI) were prepared for each type of complex (PM, WC, SC). 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 favours the interaction between the clay and the herbicide, making the release of the herbicide from these formulations slower compared with PM [9, 11]. Therefore, a range of release rates of hexazinone was expected for the three types of formulations prepared and the different herbicide loadings used.

2.4. *Batch release experiment*

The release of hexazinone into water from the commercial and organoclay formulations was monitored after adding the formulations (1 mg AI) to distilled water (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 and allowed to settle for 10 min, 2 mL of the supernatant solution was filtered, and then 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.

2.5. *Column leaching experiment*

The column leaching experiment was performed using 30 cm length × 5 cm i.d. 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 air-dried soil (490 g), saturated with 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 AI/ha (1.96 mg AI) was applied to the top of duplicate soil columns as commercial formulation or as organoclay complexes suspended in 0.01 M $CaCl_2$ (25 mL). The columns were leached with 0.01 M $CaCl_2$ at a rate of 25 mL/d until no herbicide was detected in the leachates. At the end of the leaching experiment, soil samples from the different rings (0–5, 5–10, 10–15, and 15–20 cm depth) were extracted once with a methanol + water (1 + 1 by volume) mixture (100 mL) by shaking mechanically at 20 ± 2°C for 24 h. The suspensions were centrifuged, filtered, and analysed 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 more than 95% of the herbicide freshly applied to the soil [11].

2.6. *Laboratory bioassay*

The herbicidal activity of the different hexazinone formulations was evaluated in a laboratory experiment using garden watercress (*Lepidium sativum*) seeds. Eight-centimetre diameter pots were filled with soil (220 g), saturated with water, and allowed to drain for 24 h. Fifteen seeds of garden watercress were gently distributed on the surface of each pot and incubated in a growth chamber. The pots were watered daily with distilled water (10 mL), and 1 week after sowing, the commercial or organoclay-based formulation of hexazinone was applied post-emergence at an application rate of 10 kg AI/ha. This application rate is within the range of 6–12 kg/ha recommended for field application of hexazinone [27]. Herbicidal efficacy was determined 1 week after herbicide application by visual evaluation of the weed control efficacy.

2.7. *Field study*

Hexazinone was applied at a rate of 5 kg/ha to 2 × 8 m field plots as a commercial formulation or organoclay complex (PM of HDTMA-SA, 10% AI) suspended in 4 L of water. The soil plots were not tilled before herbicide application and contained a significant amount of weeds. The herbicidal efficacy of the formulations was determined 2 weeks after herbicide application by visual evaluation of the weed control efficacy. An adjacent field plot without herbicide was used for comparison purposes. At selected times after application, triplicate soil samples were taken from different soil depths (0–10, 10–20, 20–30, and 30–50 cm) and analysed in the laboratory for their hexazinone concentration. Aliquots of soil (10 g) were extracted with a methanol + water (1 + 1 by volume) mixture (10 mL), shaken for 24 h, centrifuged, and the concentration of hexazinone determined in the supernatant solutions by HPLC.

2.8. *Herbicide analysis*

Hexazinone analysis was performed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The analysis was carried out directly on the centrifuged and filtered samples without a preconcentration step. The following conditions were used [11]: water + acetonitrile (70 + 30 by volume) eluent mixture at a flow rate of 1 mL/min, Novapack 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.

3. Results and discussion

3.1. *Organoclay–hexazinone complexes*

HDTMA-SA and PTMA-SA organoclays were selected on the basis of a previous study that revealed their different affinities for the herbicide hexazinone [11]. The greater affinity of HDTMA-SA for hexazinone compared with PTMA-SA (figure 1, table 1) can be attributed to the presence of interlamellar space available to host the herbicide molecules, which has been shown to be a critical parameter determining sorption of hexazinone and other pesticides by organoclays [11, 14, 28]. Thus, the large size of HDTMA induces its vertical orientation ($d_{001} = 2.4\,\mathrm{nm}$) in the interlayer of the highly charged SA montmorillonite, and this results in a paraffin-like structure with considerable free space between adjacent organic cations available to host hexazinone molecules [11, 13, 28]. In contrast, the small size of PTMA combined with the high surface charge density of SA results in a relatively compact packing of organic cations and a low interlamellar spacing ($d_{001} = 1.5\,\mathrm{nm}$), making the interlayer space of PTMA-SA relatively unavailable to host hexazinone molecules and limiting sorption to accessible, external sorption sites. It should be noted that under the conditions used during the preparation of HDTMA-SA, where the organic cation concentration was 120 mM, HDTMA may have existed mainly as micelles [29]. Hence, it is possible that the high sorption capacity of HDTMA-SA could also be related to being a micelle–clay system. It is also interesting to note that the effect of PTMA and HDTMA on pesticide sorption by organoclays has been shown to be strongly dependent on the surface charge density of the montmorillonite. Thus, high sorption of pesticides by low-charge montmorillonites exchanged with PTMA has been observed due to the presence of uncharged interlayer space not covered by the organic cation, which allowed interaction of the pesticide molecules with both the hydrophobic siloxane surface and the interlayer organic cation [11, 23].

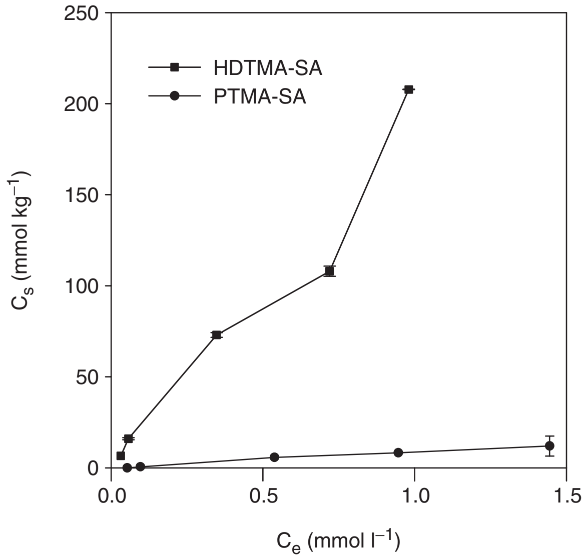

Figure 1. Hexazinone adsorption isotherms on HDTMA-SA and PTMA-SA organoclays.

As mentioned in the preceding section, three types of organoclay–hexazinone complexes (PM, WC, SC) at two different herbicide loadings (10% and 20% AI) were prepared with HDTMA-SA and PTMA-SA to test the ability of the complexes to act as CR formulations of hexazinone. The aim was to optimize the characteristics of the organoclay–herbicide complexes not only by achieving slow release of the herbicide, but also by maximizing the total amount of herbicide released from the complexes.

3.2. *Release study*

The release of hexazinone from HDTMA-SA and PTMA-SA formulations into water is compared in figure 2 with the release pattern of the commercial formulation. All formulations prepared from HDTMA-SA displayed slow release properties, whereas the commercial formulation, with 100% instantaneous release, and formulations based on PTMA-SA released the herbicide instantaneously and did not show any slow release properties (figure 2). As mentioned above, the low affinity of PTMA-SA for hexazinone (figure 1) suggests that sorption takes place mainly on accessible, external sites, and it appears that the herbicide is readily released from these sites. In contrast, the extensive retention of hexazinone by HDTMA-SA suggests entrance of the herbicide within the interlayer organic phase [11], resulting in much slower release compared with PTMA-SA.

The release patterns of HDTMA-SA complexes are characterized by an initial release ($t = 0$) that ranged from 25% to 90% of the herbicide present in the formulations and

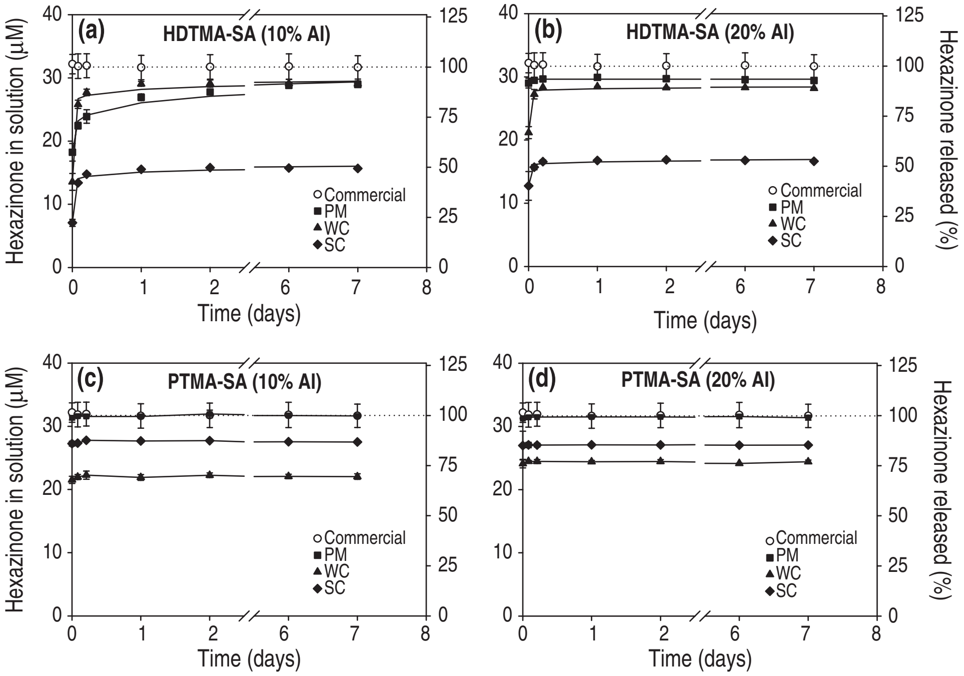

Figure 2. Hexazinone release kinetics in water from the commercial and organoclay formulations: (a) HDTMA-SA (10% AI); (b) HDTMA-SA (20% AI); (c) PTMA-SA (10% AI); (d) PTMA-SA (20% AI).

a final release ($t = 7$ d) from 50 to 90%. The release pattern for these formulations depended not only on the type of preparation but also on the herbicide loading. Thus, the initial release ($t = 0$) decreased in the order: PM > WC > SC and was lower for the complexes with 10% AI than for the complexes with 20% AI. Higher herbicide loading renders greater initial release probably as a result of saturation of sorption sites or because retention becomes weaker as the amount of herbicide on the sorbent increases. In any case, these results indicate that a range of rates and extents of hexazinone release can be achieved by selecting the type of preparation (PM, WC, or SC) and the herbicide loading in the complexes.

The high amount of hexazinone retained at the end of the experiment for some of the preparations, particularly the SC formulations (figure 2), has been attributed to entrapment of the herbicide in the organoclay interlayers as a result of both the longer time of interaction and the wetting–drying cycle carried out during the preparation of the complexes [9, 11, 13, 15, 30]. Nevertheless, it is interesting to note that for the three types of formulations prepared, the total amounts of hexazinone released from our complexes (with 10% and 20% AI) were significantly greater than those observed for similar complexes with 4% AI [11]. Thus, it appears that increasing the herbicide : organoclay ratio can be a good strategy to make the interaction of the herbicide with the organoclay less intimate and hence to maximize the release efficacy of herbicide–organoclay formulations.

3.3. *Column leaching study*

Hexazinone breakthrough curves ($\mathrm{BTC_s}$) for selected HDTMA-SA and PTMA-SA formulations are shown in figures 3 and 4. Application of the herbicide as HDTMA-SA complexes clearly resulted in a lower hexazinone concentration in leachates, flattening of the BTC, and shifting of the maximum concentration peak to larger water volumes compared with the commercial formulation (figures 3a and c). In contrast, PTMA-SA formulations only decreased the hexazinone concentrations in leachates, but did not significantly retard the movement of the herbicide through the soil column (figure 4a). The maximum concentration of hexazinone occurred in the leachates of HDTMA-SA formulations 2–3 days (50–75 mL) later compared with the commercial formulation (figure 3), and the presence of hexazinone in leachates at moderate concentrations was extended to larger volumes of water added (tailing effect observed in figures 3a and 3c for the organoclay formulations). As pointed out by Celis *et al.* [11], this is one of the most desirable features of CR formulations, since the decrease in herbicide concentration in leachates without any shift in the maximum concentration peak (figure 4a) can be an artefact due to the amount of herbicide molecules that are irreversibly entrapped by the sorbent and, therefore, are not available for leaching. In contrast, the tailing effect observed for the HDTMA-SA formulations indicates a slower movement of the herbicide through the soil profile, which is desirable to prolong the presence of the herbicide in the top layer and in turn to maximize the efficacy and reduce the risk of groundwater contamination.

Leaching results were in agreement with the release properties displayed by HDTMA-SA and PTMA-SA organoclays in the batch experiment and confirmed that PTMA-SA releases the herbicide instantaneously, whereas the release from HDTMA-SA occurs progressively. In HDTMA-SA formulations, the tailing effect

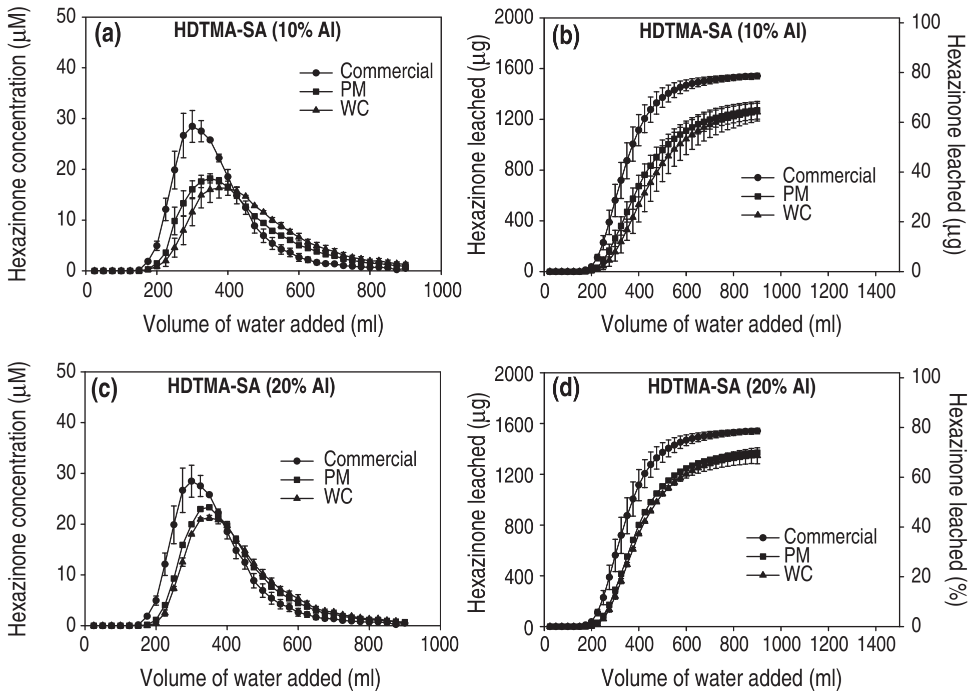

Figure 3. Hexazinone BTCs after application to soil columns as commercial and HDTMA-SA formulations: (a) relative BTCs–10%AI; (b) cumulative BTCs–10% AI; (c) relative BTCs–20% AI; (d) cumulative BTCs–20% AI.

was more pronounced for complexes with 10% AI than for those with 20% AI, especially for the WC preparation, which is in accordance with the release rates observed in the batch experiment (figure 2). Again, it seems that the leaching pattern can be controlled by varying not only the type of preparation, but also the herbicide : organoclay ratio of the complexes.

Cumulative BTCs (figures 3b, 3d, and 4b) showed total amounts of hexazinone leached that were also in agreement with the final release from the different formulations observed in the batch study (figure 2). Since negligible amounts of hexazinone remained in the soil columns at the end of the leaching experiment (extraction data not shown), the amounts of hexazinone that had 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. Nevertheless, there was little difference between the total amount of hexazinone leached for the commercial and HDTMA-SA formulations, which indicates little irreversible sorption of hexazinone to the organoclays. This is of great interest in order to minimize the amount of pesticide not released from the complexes that would result in reduced herbicidal efficacy and undesirable soil contamination. Leaching data indicate, in summary, that HDTMA-SA formulations retarded hexazinone leaching through soil while maintaining high amounts of herbicide released, and that the possibility exists to select the characteristics of the formulation to render different leaching patterns according to the desired behaviour.

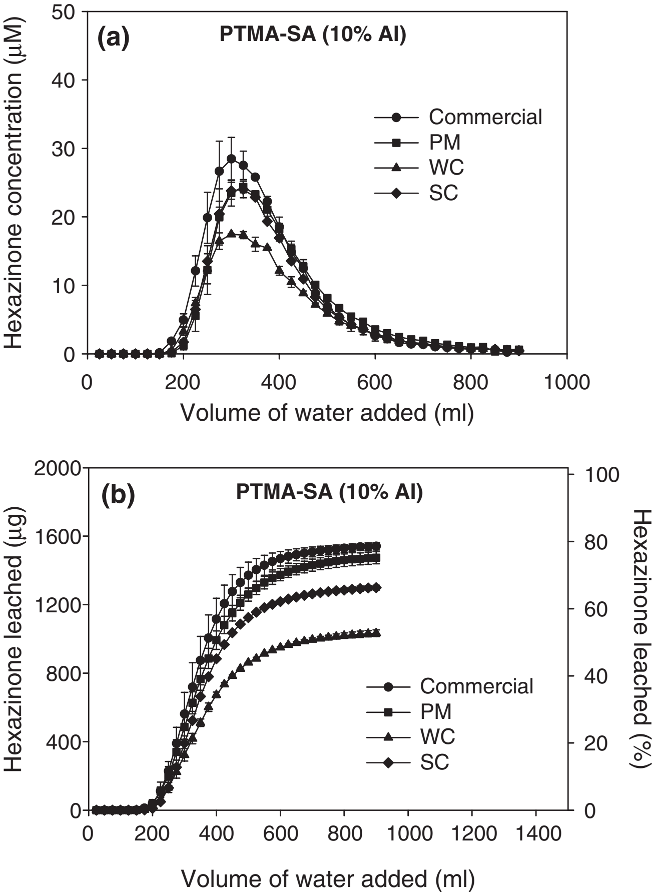

Figure 4. Hexazinone BTCs after application to soil columns as commercial and PTMA-SA formulations (10% AI): (a) relative BTCs; (b) cumulative BTCs.

3.4. *Bioassay and field study*

The herbicidal activity of hexazinone was assessed in laboratory bioassays for all formulations prepared. It was found that all organoclay formulations applied post-emergence were as effective as the commercial formulation in the control of garden watercress (*Lepidium sativum*); 100% mortality was observed after application of hexazinone either as commercial formulation or as organoclay complexes at a rate of 10 kg AI/ha (not shown). This application rate is within the range of 6–12 kg/ha recommended for field application of the herbicide [17]. These results suggest that organoclay-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 field experiment reported below further confirmed this hypothesis.

The PM preparation of HDTMA-SA with 10% AI was selected for the field experiment on the basis of its release characteristics and the simplicity of its preparation procedure. Hexazinone applied as an organoclay formulation at a rate of 5 kg AI/ha

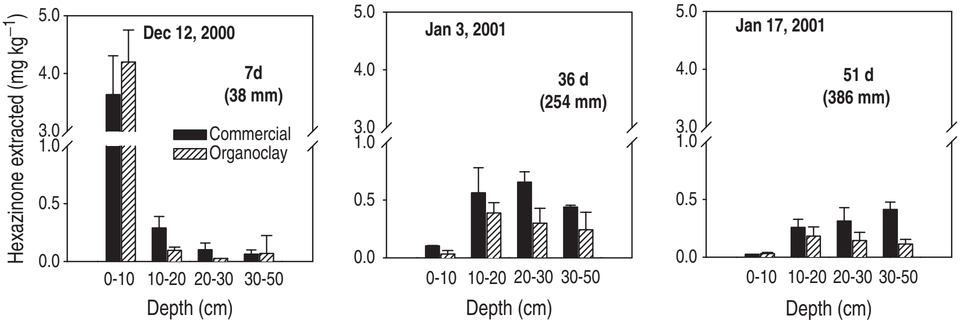

Figure 5. Hexazinone extracted from different depths of field plots after herbicide application as commercial and organoclay (PM, HDTMA-SA 10% AI) formulations. Days after herbicide application and cumulative rainfall.

had a herbicidal efficacy comparable with that of the commercial formulation. Two weeks after hexazinone application, most weeds initially present in the two field plots had been equally eliminated (not shown). In addition, soil analysis revealed that hexazinone applied as an organoclay formulation leached less than the commercial formulation (figure 5). Thus, 36 days after herbicide application, the maximum concentration of hexazinone was found at 20–30 cm depth for the commercial formulation and at 10–20 cm depth for the organoclay formulation. Similarly, 51 days after herbicide application, the maximum concentration of hexazinone was found at 30–50 cm depth for the commercial formulation but remained at 10–20 cm for the organoclay formulation. These results confirm that organoclay-based formulations can be used under field conditions at application rates within those recommended for soil application of hexazinone, reducing herbicide leaching through soil while maintaining a weed control efficacy similar to that of the currently available commercial formulation.

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