

Behaviour of an organomontmorillonite-acetochlor formulation in drained wetland soils of the Hula Valley

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SUMMARY

Weed control poses a real challenge to agriculture in general, and to agriculture on drained peatlands in particular. An understanding of the interactions between clay minerals and organic molecules has yielded effective preparations of herbicide formulations. In most cases, binding the active ingredient to a suitable organoclay-based platform enhances activity by reducing migration of the herbicide to non-target depths, or by reducing degradation of the active ingredient. In this short communication, a formulation based on an organoclay and the herbicide acetochlor is compared with a commercial formulation. Efficiency was tested in two soils from the Hula Valley: a mineral, clay-based soil (with about 4 % organic matter) and a peat-derived soil with ~20 % organic matter. Although the soils were located only two kilometres apart, completely different herbicidal activity was observed. In the mineral soil, the organoclay formulation improved the behaviour of the herbicide and prevented its leaching; whereas in the peat-derived soil, the organoclay and commercial formulations behaved similarly, and were confined to the upper soil layer. In the latter case, the penetration depth of herbicide added in the organoclay formulation might be too shallow, resulting in poor herbicidal activity. The results of this study demonstrate differences that should be considered in weed control in drained peat soils.

KEY WORDS: organoclay; acetochlor; herbicide; mineral soil; peat-derived soil

ABBREVIATIONS: a.i. : active ingredient; CEC : cation exchange capacity.

INTRODUCTION

Weed control poses a real challenge to agriculture in general, and to agriculture on drained peatlands in particular. Herbicides that work efficiently for weeks in mineral soils are completely ineffective when applied at the same rates to peat soils. For example, trifluralin is applied in peat soils at 20 % higher rates than in mineral soils. On the other hand, alachlor application is not recommended for cultivation of peanuts in Israel except in soils with high organic content, due to the danger of leaching and pollution of groundwater (Hula Valley farmers, personal communication).

Acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide] is a position isomer of the herbicide alachlor (Ahrens 1994) which is used as a pre-emergence herbicide to control grass weeds in corn and soybean (Breaux 1986). As reported in several studies, the

commercial formulation of acetochlor (emulsifiable concentrate) suffers rapid loss of herbicidal activity due to leaching to deep soil layers (El-Nahhal *et al.* 2001). Leaching of herbicides may result in groundwater contamination (USEPA 1994), which is enhanced by repeated applications by growers.

Previous studies have proposed formulations based on the interactions between clay minerals, organic chemicals and widely used pesticides, in order to reduce leaching or avoid decomposition (e.g. El-Nahhal *et al.* 1997, Nir *et al.* 2000, Casal *et al.* 2001, Carrizosa *et al.* 2004, Rytwo *et al.* 2005, Rytwo *et al.* 2008). Formulations for acetochlor were based on the preparation of a hydrophobic complex between an organic cation and the clay mineral to which the non-polar herbicide was bound (El Nahhal *et al.* 2001, Nir *et al.* 2006). Thus, the organoclay was used as an anchor to reduce the quantities of herbicide that leached with rain and irrigation.

In general, all organoclay-herbicide formulations are based on three elements (Rytwo *et al.* 2008):

- the substrate: a clay mineral that, due to its special mineralogical structure, offers several binding sites contributing to the interactions with organic molecules;
- the organic molecule bound to the clay mineral ("modifier"): usually an organic cation with a hydrophobic moiety to increase the affinity of non-polar herbicides to the organoclay; and
- the herbicide: an organic molecule that has a biocidal effect, aimed at improving the quality or yield of the crop where applied, which is usually combined by chemical interaction with the platform prepared from the clay mineral and organic modifier.

In all developed formulations, the rationale is to reduce the amounts of herbicide applied, in order to both protect the environment and reduce costs. However, all formulations should take into consideration soil composition since, for instance, large amounts of organic matter may influence the behaviour of the herbicide.

This study presents the activity of an organoclay-acetochlor formulation, which had previously been successfully tested (El-Nahhal *et al.* 2001), in one mineral and one peat-derived soil collected from sites located two kilometres apart in the Hula Valley.

METHODS

Mineral and peat-derived soils were collected from two sites in the Hula Valley. The first (33° 8' 54" N, 35° 34' 17" W) was "brown alluvium" mineral soil from the eastern edge of the valley, and the second (33° 6' 45.36" N, 35° 35' 16" W) was a "peat" soil from the area which was a marsh until Lake Hula was drained in the mid-twentieth century (see maps in Litaor *et al.* 2011). At each site, soil sampling was performed by digging out approximately 20 litres of soil from 20–40 cm depth with a spade.

The soil samples were air-dried and sieved through a 2-mm sieve to separate gravel particles from fresh organic matter. The organic matter content was evaluated by the dichromate method (Nelson & Sommers 1996), and soil texture was determined by the hydrometer method (Gee & Bauder 1982). Green foxtail (*Setaria viridis* (L.) Beauvois) seeds served as the test plants.

The "commercial" formulation (emulsifiable concentrate) of acetochlor (*Harness*; Monsanto Chemicals, 900 g a.i. kg⁻¹) was used as purchased. Its application was compared with an acetochlor

formulation prepared at the Robert H. Smith Faculty of Agriculture, Food and Environment of the Hebrew University, as reported in El-Nahhal *et al.* (2001). The formulation (denoted "Rehovot" formulation) was based on an organoclay prepared from Wyoming SWy-2 montmorillonite with phenyl-trimethyl-ammonium (PTMA) adsorbed at 0.5 mol_c kg⁻¹ clay (about 60 % of the CEC of the clay) and 40 g acetochlor kg⁻¹ formulation.

PVC columns made from 35 cm lengths of 7.62 cm (3" nominal) water pipe (internal diameter 7.35 cm, cross section 42.49 cm²) were used to evaluate herbicide leaching in both soils, as described by El-Nahhal *et al.* (2000). The columns were cut lengthwise and re-sealed with adhesive tape, as shown in Figure 1a. A filtering net was placed at the bottom of each column to allow excess water to flow out. The columns were pre-irrigated at 480 m³ ha⁻¹ (equivalent to 48 mm of rain) and left for three days to reach field water content. Irrigation was performed using Netafim (Hatzerim, Israel) pressure-compensated 2 l h⁻¹ drippers, through filter papers to keep the surfaces of the columns uniform (Figure 1b). After three days, the column surfaces were sprayed with the recommended field rate (2.0 kg a.i. ha⁻¹) of either commercial or Rehovot herbicide formulation using an atomiser. The columns were then re-irrigated, using the same irrigation system, at 500 or 750 m³ ha⁻¹ (equivalent to 50 and 75 mm of rain, respectively). Irrigation times were calculated according to the areas of the columns and the irrigation rates of the drippers. A computerised valve was programmed to work in cycles of 1 minute open : 15 minutes closed. After six cycles (200 cm³ for each column), the drippers were removed from some of the columns, and the remainder were irrigated with an additional four cycles (to a total of 333 cm³ per column). Thus, the "50 mm treatment" actually received 47 mm of water, and the "75 mm treatment" received 78 mm of water. Three columns were prepared for each treatment and three additional columns served as controls (i.e. 15 columns in total). Control columns were irrigated as the "75 mm treatment".

After 48 hours of equilibration, the PVC columns were laid on their sides and opened to form 35-cm-long "troughs" (Figure 1c). Green foxtail seeds were sown in two rows along the length of each trough. All columns were subsequently irrigated once a day for 30 minutes with a microsprinkler to ensure development of the foxtail plants (Figure 1d). Shoot length was measured after two weeks, and relative growth inhibition at a given soil depth along the column length was calculated by comparing the shoot lengths in treated samples and controls at the same depths.

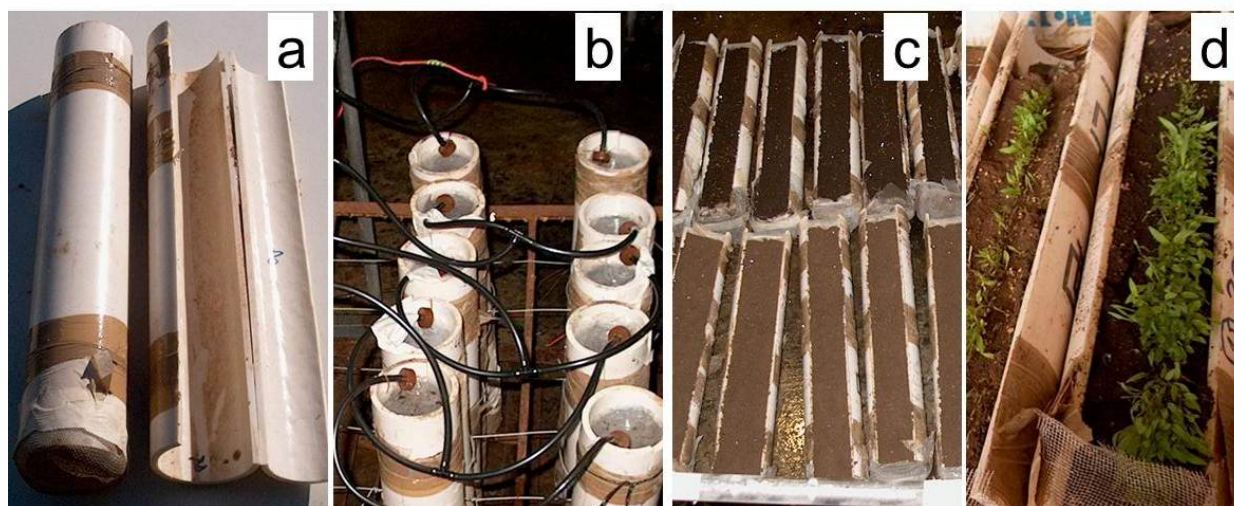


Figure 1. Experiment preparation stages: (a) a closed and an open column; (b) columns with irrigation drippers; (c) opened columns after sowing; and (d) foxtail plants growing in the open columns. In (c) the dark soil (top row) is peat, and the columns in the bottom row contain mineral soil.

RESULTS

The textures and organic matter compositions of the soils are given in Table 1. Based on texture, the peat-derived soil is classified as silt loam and the mineral soil as clay (Radojevic & Bashkin 1999).

Since foxtail plants are sensitive to acetochlor, shoot lengths provide a direct indication of the presence of herbicide at each specific depth. Figure 2 shows shoot length as a function of depth in the columns, after spraying with herbicide followed by the 50-mm and 75-mm irrigation treatments; and Table 2 shows depths of relative inhibition, as compared with the control columns.

In peat soil with 50 mm irrigation, the commercial formulation completely prevented weed growth to about 4 cm depth, whereas the organoclay (Rehovot) formulation inhibited growth but did not prevent it. Marked leaching was not observed for either formulation, and there was almost no growth

inhibition at about 10 cm depth. In mineral soil with 50 mm irrigation, both formulations prevented growth for about 2 cm, but while the commercial formulation leached downwards and had a considerable influence even at 20 cm depth, the influence of the Rehovot formulation was confined to the top 9 cm, showing an environmentally efficient behaviour that could prevent leaching of acetochlor to the sub-soil and groundwater.

Similar trends were observed with 75 mm irrigation. In the peat soil, the commercial formulation showed good weed control in the uppermost 6–8 cm and no herbicide was found beyond 12 cm depth; whereas the organoclay formulation did not leach below 5 cm but showed only 2 cm of weed control. In the mineral soil, the commercial formulation leached to almost 30 cm, implying highly hazardous environmental behaviour, whereas the organoclay formulation was still confined to the upper 10 cm.

Table 1. Organic matter content, textures and classifications of the soils used.

soil type	location		organic matter (%)	clay (%)	silt (%)	sand (%)	classification*
	latitude (°N)	longitude (°W)					
peat	33.1126	35.5877	19.4	6.0	53.0	41.0	silt loam soil
mineral	33.1482	35.5713	4.5	56.8	16.2	27.0	clay soil

*according to USDA classification (Radojevic & Bashkin 1999).

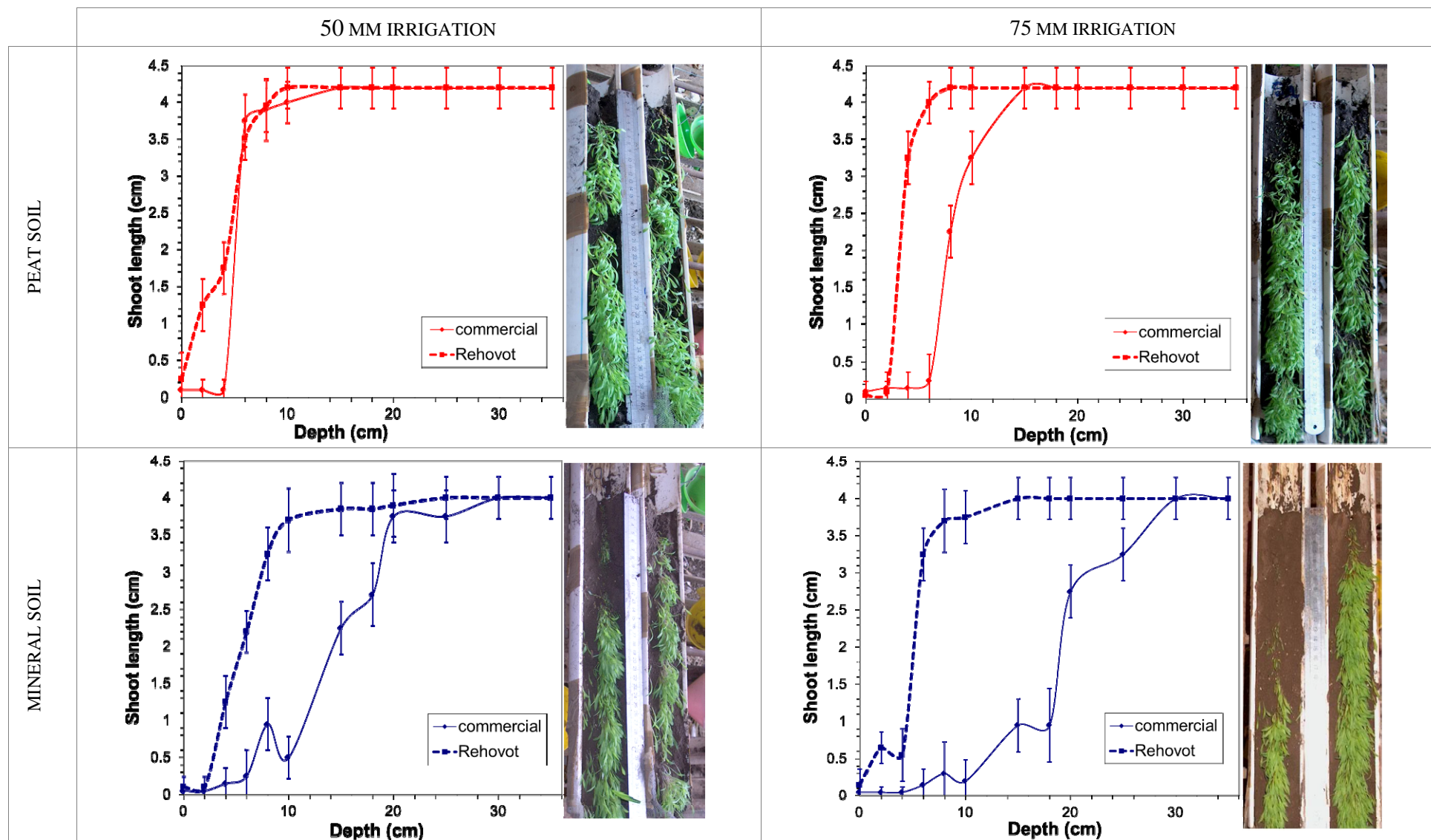


Figure 2. Shoot length as a function of depth along the column in peat soil (above) and mineral soil (below), following 50 mm (left) and 75 mm (right) of irrigation. All columns were sprayed with the equivalent of $2.0 \text{ kg acetochlor ha}^{-1}$, in a commercial or organoclay-based (Rehovot) formulation.

Table 2. Depths of relative inhibition (in cm). Acetochlor was applied at a rate of 2 kg ha⁻¹ in a commercial (comm.) or organoclay-based (Reh.) formulation.

soil type	peat				mineral			
irrigation	50 mm		75 mm		50 mm		75 mm	
formulation	comm.	Reh.	comm.	Reh.	comm.	Reh.	comm.	Reh.
depth of complete inhibition	4	0	6	2	2	2	10	4
depth of 75% inhibition	5	2	7	3	14	5	19	5
depth of 25% inhibition	6	4	9	4	19	7	24	6
depth of no inhibition	10	8	12	5	26	9	29	11

DISCUSSION

It should be noted that the desired herbicide behaviour is a compromise between the need to reach the roots in order to perform the herbicidal action, and the requirement to avoid leaching to depths where herbicide activity is not needed. Several different thresholds can be found in the literature (El-Nahhal *et al.* 1999, 2005), but it is clear that 2 cm of activity might yield inefficient weed control, whereas more than 15 cm of activity is certainly excessive and may indicate hazardous leaching behaviour such that herbicide eventually reaches the groundwater. Considering these limits, the results can be interpreted as described below.

Although the organoclay formulation showed optimal activity in the mineral soil at both irrigation rates, it might yield ineffective weed control in organic (peat-derived) soils because it acts only in the uppermost 1–2 cm of the soil. Such behaviour can be explained by sorption of the organoclay-herbicide compound onto organic matter in the peat, which almost completely prevents movement of the herbicide in the soil and thus the possibility of its reaching the weed roots. On the other hand, the commercial formulation is environmentally unacceptable in mineral soils because leaching to depths of more than 20 cm can be hazardous to soil

and water; but in the peat soil, this formulation shows relatively good performance with activity confined to the top 10–15 cm, even at the higher irrigation rate.

Thus, herbicide formulations must be specifically tailored to soil types. Whereas the commercial acetochlor formulation may be efficient in peat soils, the organoclay formulation can deliver a solution for weed control in mineral soils that poses no environmental threat to the groundwater. Considering that the soils tested in this study occurred at locations only two kilometres distant from one another, precision agriculture might pose a difficult challenge for farmers aiming to adapt herbicide treatments to specific soil conditions in order to optimise environmentally oriented weed control, since herbicide formulations that work efficiently in mineral soils may not be efficient in drained peatlands.

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REFERENCES

- Ahrens, H.W. (ed.) (1994) *Herbicide Handbook*, Seventh Edition, Weed Science Society of America, Champaign, IL, 352pp.
- Breaux, E.J. (1986) Identification of the initial metabolites of acetochlor in corn and soybean seedlings. *Journal of Agriculture and Food Chemistry*, 34, 884–888.
- Carrizosa, M.J., Koskinen, W.C., Hermosin, M.C. & Cornejo, J. (2004) Interactions of two sulfonylurea herbicides with organoclays. *Clays and Clay Minerals*, 52, 643–649.
- Casal, B., Merino, J., Serratos, J.M. & Ruiz-Hitzky, E. (2001) Sepiolite based materials for the photo and thermal stabilization of pesticides. *Applied Clay Sciences*, 18, 223–231.
- El-Nahhal, Y., Lagaly, G. & Rabinovitz O. (2005) Organoclay formulations of acetochlor: effect of high salt concentration. *Journal of Agricultural and Food Chemistry*, 53, 1620–1624.
- El-Nahhal, Y., Nir, S., Margulies, L. & Rubin, B. (1999) Reduction of photodegradation and volatilization of herbicides in organo-clay formulations. *Applied Clay Science*, 14, 105–119.
- El-Nahhal, Y., Nir, S., Polubesova, T., Margulies, L. & Rubin, B. (1997) Organo-clay formulations of alachlor: reduced leaching and improved efficacy. *Proceedings of the Brighton Crop Protection Conference—Weeds*, 1, 21–26.
- El-Nahhal, Y., Nir, S., Serban, C., Rabinovitch, O. & Rubin, B. (2000) Montmorillonite-phenyltrimethylammonium yields environmentally improved formulations of hydrophobic herbicides. *Journal of Agricultural and Food Chemistry*, 48, 4791–4801.
- El-Nahhal, Y., Nir, S., Serban, S., Rabinowitz, O. & Rubin, B. (2001) Organoclay formulation of acetochlor for reduced movement in soil. *Journal of Agricultural and Food Chemistry*, 49, 5364–5371.
- Gee, G.W. & Bauder, J.W. (1982) Particle-size analysis. In: Klute, A. (ed.) *Methods of Soil Analysis: Part 1, Physical and Mineralogical Properties*. Second Edition, ASA/SSSA, Madison, WI, 383–411.
- Litaor, M.I., Reichmann, O. & Shenker, M. (2011) Genesis, classification and human modification of peat and mineral-organic soils, Hula Valley, Israel. *Mires and Peat*, 9(01), 1–9.
- Nelson, D.W. & Sommers, L.E. (1996) Total carbon, organic carbon and organic matter. In: Sparks, D.L. (ed.) *Methods of Soil Analysis: Part 3, Chemical Methods*. ASA/SSSA, Madison, WI, 961–1010.
- Nir, S., El-Nahhal, Y., Undabeytia, T., Rytwo, G., Polubesova, T., Mishael, Y., Rabinovitz, O. & Rubin, B. (2006) Clays and pesticides. In: Bergaya, F., Theng, B.K.G. & Lagaly, G. (eds.) *Handbook of Clay Science*, Elsevier Limited, Amsterdam, The Netherlands, 685–699.
- Nir, S., Undabeytia, T., Marcovich, D., El-Nahhal, Y., Polubesova, T., Serban, C., Rytwo, G., Lagaly, G. & Rubin, B. (2000) Optimization of sorption of hydrophobic herbicides on montmorillonite preadsorbed by monovalent organic cations: interaction between phenyl rings. *Environmental Science & Technology*, 34, 1269–1274.
- Radojevic, M. & Bashkin, V.N. (1999) *Practical Environmental Analysis*, The Royal Society of Chemistry, Cambridge, UK, 466 pp.
- Rytwo, G., Gonen, Y. & Afuta, S. (2008) Preparation of berberine-montmorillonite-metolachlor formulation from hydrophobic/hydrophilic mixtures. *Applied Clay Science*, 41, 47–60.
- Rytwo, G., Gonen, Y., Afuta, S. & Dultz, S. (2005) Interactions of pendimethalin with an organo-montmorillonite complex. *Applied Clay Sciences*, 28, 67–77.
- USEPA (1994) *Questions and Answers, Conditional Registration of Acetochlor*. U.S. Environmental Protection Agency, Washington DC.

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