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Slow diuron release formulations based on clay–phosphatidylcholine complexes

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ABSTRACT

Slow release formulations of the herbicide diuron were designed to reduce the risk of water pollution resulting from conventional formulations. The new formulations were based on herbicide incorporation in phosphatidylcholine (PC) vesicles that were sorbed on the clay mineral montmorillonite. The active ingredient contents of the formulations reached up to 28% w:w. Thermal analysis revealed that the closely packed arrangement of PC on the clay enhanced diuron sorption by disrupting the interactions among PC molecules. Adsorption experiments using diuron were performed in soils with different physico-chemical properties to evaluate the relationship between the sorption and the mobility of the herbicide. In soil column experiments with sandy soil, the herbicide in PC–clay-based formulations mainly accumulated in the top soil, and there was a one-third reduction in leaching compared to the commercial formulation. The differences in leaching (compared to the commercial formulation) were lower when using loam soil due to its higher sorption of the herbicide and hysteresis effects. In the sandy soil, bioassay experiments showed a higher herbicidal activity in the top-soil layer for the PC–clay formulations than for the commercial formulation. Therefore, PC–clay formulations of this herbicide can be used at lower doses than recommended, thereby reducing the environmental risks associated with the application of diuron formulations.

1. Introduction

Clays and clay minerals are materials with high sorption capacities and colloidal properties that render them suitable for the design and preparation of pesticide formulations (Lagaly, 2001). Clay minerals have been examined as potential formulants in slow release formulations (SRFs) of several herbicides (Fernández-Pérez et al., 2004; Maqueda et al., 2008, 2009). Slow release formulations are aimed at maintaining bioefficacy while reducing the loss of active ingredients due to transfer and dissipation mechanisms, that result in the application of larger herbicide doses to control weeds and pests.

Clay minerals such as bentonite, hectorite and attapulgite, are used in crop protection products as rheological modifiers. The clay concentration depends on the type of formulation as follows: 2 to 10 g/L in suspension concentrates, 1 to 10 g/L in suspo-emulsions, and 2 to 10 g/L in flowables for seed treatments. Formulated products also contain surfactants which are included to enhance herbicide penetration into the foliar system of the plant, to increase the stability of the suspensions and to improve the physical properties of the formulated products (e.g., wetting, antifoaming, and anticaking agents).

Because of the simultaneous presence of clay minerals and surfactants in crop protection products, recent research has focused on the compatibility of clay mineral–surfactant systems for use in slow release formulations (SRFs). Most studies have focused on the use of the clay mineral montmorillonite and quaternary ammonium surfactants. These surfactants are pre-adsorbed on the clay mineral, transforming the clay surface from hydrophilic to hydrophobic and improving the retention of non-ionic herbicides (Polubesova et al., 2002; Undabeytia et al., 2000).

The herbicide affinity of the modified clay is a function of surfactant loading, the clay mineral charge, and the structural compatibility between the exchanged organic cation and the herbicide molecules (Cornejo et al., 2008; Nir et al., 2000).

Another approach recently developed for SRFs is the encapsulation of the herbicide into structures formed by surfactants in solution (micelles or vesicles) and the subsequent, the adsorption of micelles and vesicles containing herbicide onto montmorillonite (Mishael et al., 2002a,b; Undabeytia et al., 2003). The active ingredient (*a.i.*) content can reach high values, in some cases approaching those of commercial products. However, an optimal surfactant/clay ratio is required so that the surfactant is mostly sorbed as vesicles or micelles without prior decomposition into monomers on the clay surface (Undabeytia et al., 2004).

Quaternary ammonium surfactants that form vesicles and micelles in solution have proved effective in reducing leaching and enhancing the bioactivity of sulfonylurea herbicides, such as sulfometuron and sulfosulfuron (Mishael et al., 2002b, 2003; Undabeytia et al., 2003), and the herbicides metolachlor and sulfentrazone (Ziv and Mishael, 2008). Recently, this approach has been successfully modified by replacing quaternary ammonium salts with the natural

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surfactant phosphatidylcholine (PC) (Sánchez-Verdejo et al., 2008a,b; Undabeytia et al., 2010). The advantage of these formulations is that the formulants used (PC and clay) are nontoxic, indicated by their EPA-approval as substances of minimal toxicological risk.

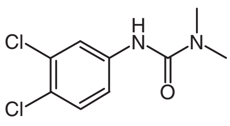
Encapsulation of the active chemical within PC vesicles involves specific interactions between the headgroups of PC molecules and the functional groups of the herbicide molecules (Sánchez-Verdejo et al., 2008b). Thus, the success of this approach strongly depends on the molecular structure of the herbicide. The present study examines the validity of this approach for phenylurea herbicides by focusing on the diuron herbicide as a model molecule. Diuron is a widely used herbicide frequently encountered in ground- and surface waters (Gregoire et al., 2010; Postigo et al., 2010). PC–clay formulations of diuron were prepared and characterized by thermal analysis methods and tested to determine their effects on diuron leaching in soils with different physico-chemical properties. Soil adsorption–desorption experiments were previously performed to determine the factors affecting diuron behavior in different soils.

2. Materials and methods

2.1. Materials

Wyoming Na-montmorillonite (SWy-2, cation exchange capacity 0.8 mmol/g) was obtained from the Source Clays Repository of The Clay Minerals Society (Columbia, MO). Phosphatidylcholine (SPC-3; 74% distearoyl-PC and 26% 1-palmitoyl-2stearoyl-PC) were supplied by Lipoid GmbH (Ludwigshafen, Germany). High Performance Liquid Chromatography (HPLC)-grade-methanol and diuron were purchased from Sigma-Aldrich (Sigma Chemical Co., St Louis, MO), and HPLC grade-acetonitrile was obtained from Teknokroma S.A. (Barcelona, Spain). The commercial formulation of diuron (Diurokey, 80% w:v) was supplied by Industrial Química Key S.A. (Lérida, Spain). Fig. 1 shows the structural formulas of PC and diuron. The dimensions of the diuron molecule are as follows: 1.29 nm in length, 0.77 nm in width and 0.74 nm in height (López-Ramón et al., 2007).

All of the soil samples were collected from the soil surface (0 to 20 cm) and passed through a 2-mm sieve before use. Soils were classified as Aquic Haploxeralfs (P44 soil), Chromic Haploxererts (TM soil), Alfic Dystrict Eutrochrepts (LM soil) and Typic Xeropsamments (AR soil). They were analyzed for their physico-chemical and microbiological properties (Table 1) according to methods described by Sopeña et al. (2008) and Undabeytia et al. (2002). A semiquantitative estimation of the clay minerals was performed using the methodology proposed by Stokke and Carson (1973) (Table 2).



Diuron (DR)

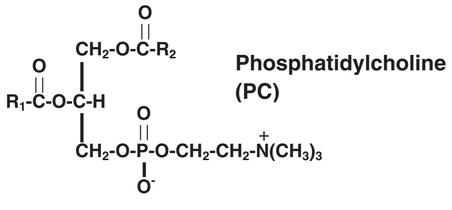


Fig. 1. Structural formulas of the diuron herbicide and the lipid PC.

Table 1
Properties of the studied soils.

	AR	P44	LM	TM
OM (g kg^{-1})	7.9	14.0	14.1	17.6
CEC ($cmol_c$ kg^{-1})	4.8	7.8	12.4	39.0
Carbonate (g kg^{-1})	69.0	<0.1	<0.1	241.0
pH	8.0	5.5	6.0	8.0
Sand (%)	87.6	49.8	16.7	2.7
Silt (%)	4.0	34.5	58.6	31.5
Clay (%)	8.4	15.7	24.7	65.9
Total Fe_2O_3 (g kg^{-1})	11.4	46.1	356.8	43.9
Amorphous Fe_2O_3 (g kg^{-1})	0.4	1.9	8.43	0.8
Total Al_2O_3 (g kg^{-1})	53.2	111.8	148.2	116.4
Amorphous Al_2O_3 (g kg^{-1})	0.2	1.0	8.5	3.5
Total MnO (g kg^{-1})	<0.1	0.6	21.9	0.7
Amorphous MnO (g kg^{-1})	<0.1	0.1	9.8	0.2
S_{BET} (m^2/g)	1.5	7.2	42.6	69.8

2.2. Preparation of herbicide–PC–clay formulations

PC formulations of diuron were prepared by dissolving the herbicide in a solution of 6 mM PC via sonication and subsequently adding the suspension to montmorillonite. The concentrations of herbicide added were 3 and 8 mM, whereas the clay concentrations were 1.6 and 5 g/L. After shaking for 24 h, the suspensions were centrifuged at 20,000 *g* for 10 min, and the supernatant was analyzed to quantify the remaining herbicide. The pellets obtained from centrifugation were freeze-dried to yield PC–clay formulations. A nomenclature for PC–clay formulations was introduced, whereby the first letters indicate the herbicide (DR), the first number denotes the initial herbicide concentration, and the second number represents the clay concentration. Similarly, PC–clay complexes were prepared in the absence of herbicide and denoted by PC/6/Y, where Y denotes the clay concentration used.

2.3. Herbicide analysis

Diuron was analyzed by HPLC (Shimadzu Model 10A) employing a PDA detector. The reverse phase column was a 15 cm Kromasil 100C18. The flow rate was 1.0 mL min^{-1}. The mobile phase was 60% acetonitrile and 40%: water. The wavelength was set at 230 nm, and the retention time of diuron was 3.04 min.

2.4. Thermal analysis methods

For PC–clay complexes and herbicide formulations, thermogravimetry (TG/DTG) and evolved gas analysis (EGA) measurements were carried out under a flow of argon at a heating rate of 6 K/min with a SETARAM equipment (model SETSYS Evolution). For each measurement, the sample amount was 0.01 g.

Emanation Thermal Analysis (ETA) measurements (Balek and Tölgyesy, 1984) were performed on samples under a flow of argon (flow-rate 40 ml/min) at a heating rate of 6 K/min with a modified NETZSCH ETA DTA 404 equipment.

ETA (Balek, 1978; Ziegler et al., 1985) involves measurements of the radon release rate from previously labeled samples. Samples for ETA were labeled with an acetone solution containing traces

Table 2
Clay mineralogy of the soil clay fraction.[a]

Soil	S%	I%	K%	V%
AR	–	25	52	–
P44	–	58	42	–
LM	–	45	30	25
TM	70	15	15	–

[a] S: smectite, I: illite, K: kaolinite, V: vermiculite.