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Effect of addition of HPBCD on diuron adsorption–desorption, transport and mineralization in soils with different properties

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ABSTRACT

The influence of different soil properties on diuron adsorption and the effect of hydroxypropyl-β-cyclodextrin (HPBCD) on its desorption, leaching, and mineralization have been investigated. The significant variables on adsorption were organic matter (OM) content, aluminum oxides, and clay fraction. Diuron desorption from soils presents negative hysteresis when HPBCD solutions were used as an extractant, in comparison to the positive hysteresis when using $Ca(NO_3)_2$ solutions. Therefore, higher amounts of diuron were desorbed by HPBCD due to the formation of an inclusion complex that causes an increase in its solubility. However, the application of HPBCD in columns of selected soils did not cause increased leaching of the herbicide. Finally, the presence of HPBCD shows clearly an increase in the rate of mineralization of diuron in contaminated soils and a drastic reduction of DT_{50} values due to its increasing bioavailability. HPBCD is proposed as an efficient tool for diuron soil bioremediation.

1. Introduction

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is an herbicide belonging to the phenylamide family and the subclass of phenylurea (Giacomazzi and Cochet, 2004). This substituted urea herbicide inhibits photosynthesis by preventing oxygen production and blocks the electron transfer at the level of photosystem II of photosynthetic micro-organisms plants. This compound is used to control a wide variety of annual and perennial broadleaf and grassy weeds on many agricultural crops such as fruit, cotton, sugar cane, alfalfa, and wheat at 0.6–4.8 kg ha^{-1}, as well as on non-crop areas such as roads, garden paths, and railway lines at 3–30 kg ha^{-1} (Tomlin, 2000). Dispersion of this compound in agriculture leads to pollution of the aquatic environment by runoff (Louchart et al., 2001; Thurman et al., 2000) and leaching (Inoue et al., 2014; Langeron et al., 2014). Diuron is considered a Priority Hazardous Substance by the European Commission (Directive 2000/60/EC). Understanding the fate of a pesticide in the soil environment requires knowledge of both its adsorption capacity and degradation rate. The processes of adsorption and degradation have often been found to be correlated since degradation can be restricted to the soil solution, and hence sorbed molecules may be protected from microbial attack, what has been proved by several studies for a broad range of chemicals, including pesticides (Kah and Brown, 2007; Quintero et al., 2005) and various organic contaminants (Braida et al., 2004; Stokes et al., 2005).

Environmental microbiologists define bioavailability as “the contaminant fraction which represents the accessibility of a chemical to a living organism for assimilation, degradation and ecotoxicity expression” (Semple et al., 2007). The bioavailability of organic pollutants governs their ecotoxicity and degradation in contaminated soils. This relationship is apparent in soils with high organic matter content, in which easily biodegradable organic compounds persist for long periods even under conditions favorable for biodegradation (Alexander, 1999). Consequently, the bioavailability of contaminants varies with the type, nature of contaminants and environmental factors such as the composition of soil (clay fraction and organic matter content mainly), the residence time of the chemical in soil, the desorption rate, and the nature of the microorganisms which influence the bioavailability and the biodegradation and toxicity of sorbed compounds. Biodegradation is by far the best and most likely the only environmentally means of detoxification of organic contaminants in soil and water except when biodegradation leads to the formation of toxic and/or persistent metabolites.

Cyclodextrins (CDs) are cyclic organic compounds obtained by enzymatic transformation of starch. These molecules exhibit a cavity with a hydrophobic character, whereas the exterior is strongly hydrophilic. This peculiar structure allows organic molecules to be included in the cavity via non covalent bonds to form inclusion complexes. The complexation of pesticides and other contaminants with CDs may result in considerable improvement of their properties, such as enhancement of solubility and bioavailability (Yu et al., 2015; Bilensoy, 2011; Morillo, 2008; Manolikar and Sawant, 2003). A large number of papers in which the complexation with CDs is studied using pesticides that present problems can be found, from both agricultural and environmental

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points of view (Pérez-Martínez et al., 1999; Villaverde, 2007; Villaverde et al., 2013a, 2013b; Morillo et al., 2012; Sánchez-Trujillo et al., 2013, 2014). CDs have the tendency to form inclusion complexes by reversibly incorporating a nonpolar compound into their hydrophobic central cavities (Villaverde et al., 2006). The use of CD solutions as enhancers in pollutant dissipation in soil has been postulated as a promising in situ decontamination tool because it enhances pesticide soil desorption. Previously, our group has reported numerous results using different types of CD solutions for enhancing soil desorption of different herbicides (Villaverde et al., 2005; Villaverde, 2007; Pérez-Martínez et al., 2000). Also, in the presence of the HPBCD solution, almost complete disappearance of diuron was observed at the end of the experiment (only 6.85% of the initial amount remained) when an exogenous bacterial consortium was applied (Villaverde et al., 2012).

Therefore, the aim of this work was to gain insight into the fate and behavior of diuron in the soil–water system, regarding its adsorption–desorption, transport, and mineralization in absence or in presence of HPBCD (hydroxypropyl-β-cyclodextrin) to determine if HPBCD can be used for diuron decontamination in soils.

2. Materials and methods

2.1. Materials

Technical grade (98%) diuron [*N*-(3,4-cichlorophenyl)-*N*,*N*-dimethyl-urea] was provided by PRESMAR S. L. Radiolabelled [ring-U-14C]-diuron was purchased from the Institute of Isotopes (Budapest, Hungary) with specific activity of 1332 MBq mmol^{-1}, chemical purity of 99.9% and radiochemical purity of 100%. The cyclodextrin (CD) hydroxypropyl-β-CD (HPBCD) was purchased from Cyclolab, Budapest, Hungary. Seven different soils from southwestern Spain were employed in this study. Soil analysis were performed on air-dry soil sieved at 2 mm. They were taken from the superficial horizon (0–20 cm) and analyzed for pH in saturated paste, total carbonate content, particle size distribution, and organic matter content. The amorphous and organically bound iron, manganese, and aluminum oxides were determined using ammonium oxalate-oxalic acid (McKeague et al., 1971). These properties are shown in Table 1.

2.2. Diuron adsorption–desorption studies in soils

Triplicate batch adsorption experiments were performed by mixing 10 g (dry mass) of the soil with 10 mL solution containing 0.01 M $Ca(NO_3)_2$ as background electrolyte, 200 mg L^{-1} $HgCl_2$ to prevent bacterial growth, and various concentrations (2, 5, 10, 15, and 20 mg l^{-1}) of diuron, in 50 mL polypropylene centrifuge tubes. The samples were shaken for 72 h at 20 ± 1 °C (on an orbital shaker). This time of reaction was chosen from preliminary kinetic studies (not shown), which showed that adsorption had reached pseudoequilibrium. After shaking, the suspensions were centrifuged (12,000*g*) and the concentration of diuron in the supernatant was determined by using a Shimadzu HPLC equipped with UV detector. The conditions used were as follows: mobile phase, acetonitrile/water (60:40); flow rate, 1.00 mL/min; temperature, 30 °C; chromatographic column, kromasil C18 reverse phase; wavelength, 230 nm; and retention time, 2.5 min. The difference in herbicide concentration between the initial and final equilibrium solutions was assumed to be due to sorption, and the amount of diuron was retained by the adsorbent calculated. Sorption isotherms were fitted to the logarithmic form of the Freundlich equation:

$$\log Cs = \log K_f + n \log Ce$$

where Cs (μmol kg^{-1}) is the amount of the herbicide sorbed at the equilibrium concentration Ce (μmol l^{-1}), and K_f and n are constants that characterize the relative sorption capacity and the sorption intensity, respectively, for the herbicide. The normalized distribution coefficient (K_{foc}) of organic carbon (OC) was calculated from the K_f values ($K_{foc} = K_f/OC \times 100$). The organic carbon content (OC) was determined as follows: $OC\% = 0.58 \times OM\ (\%)$. K_{foc} is often used in the discussion of sorption of nonpolar hydrophobic compounds, the concept being compatible with the idea of organic carbon (OC) having the same affinity for a nonpolar compound, independent of the source of OC.

Desorption experiments were performed after adsorption equilibrium had been reached for the point corresponding to diuron initial concentration of 10 mg l^{-1} by removing half of the supernatant after centrifugation, replacing it by 5 mL of the extractant solution, allowing equilibration for an additional 24 h period, and after that, operating as in the adsorption experiment. This process was repeated twice. Desorption experiments were carried out using 0.01 M $Ca(NO_3)_2$ solution or HPBCD × 10 (HPBCD equivalent to 10 times the diuron initially added to soil, 4.29×10^{-3} mmol). The percentage of diuron desorbed with respect to that previously adsorbed during adsorption process (%D) was calculated for all the desorption experiments.

2.3. Leaching experiments in soils columns

Leaching experiments were done in duplicate for two selected soils (soil 1 and soil 7), which were chosen for being the most different in their properties from each other. Homogeneous soil columns were prepared by packing the soil gently and uniformly in 16 cm long methacrylate tubes of 3.0 cm internal diameter. The lower end was covered with nylon tissue and padded with a thin layer of glass wool (0.5 g) to hold the soil firmly into the column. Each column was filled with 125 g of soil 1 and 167 g of soil 7 to achieve 16 cm occupied by soil. The top of these columns was covered with glass wool to prevent disturbance of the soil by the input liquid.

In a preliminary experiment, soil columns were first saturated by capillarity with distilled water to obtain a soil moisture content of 100% of the field capacity. The difference between the weight of the saturated soil column and its dry weight was used to determine the pore volume (35 mL for soil 1, 47 mL for soil 7).

Table 1
Different properties of the soils studied.

Soil	1 (silt loamy)	2 (silt loamy)	3 (clay)	4 (sandy loamy)	5 (loamy)	6 (silt loamy)	7 (sandy)
OM (%)	3.37	2.13	1.76	1.75	1.56	1.41	0.20
CO_3^{-2} (%)	1.60	2.00	24.1	27.5	0.00	0.00	11.0
pH	6.23	6.97	8.00	8.73	5.50	6.00	8.58
Sand (%)	24.2	31.6	2.70	59.4	49.8	16.7	95.3
Silt (%)	59.4	53.6	31.5	15.9	34.5	58.6	4.10
Clay (%)	16.4	14.8	65.9	24.6	15.7	24.7	0.60
Amorphous Fe_2O_3 (g kg^{-1})	5.95	14.6	1.56	0.79	2.23	11.6	0.16
Amorphous Al_2O_3 (g kg^{-1})	8.56	26.2	0.33	0.17	0.34	17.5	0.18
Amorphous MnO (g kg^{-1})	8.00	13.9	3.13	1.03	0.98	11.1	0.80
Total amorphous oxides (TAO)(g kg^{-1})	22.5	54.8	5.03	1.99	3.56	40.2	1.53