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Assisted attenuation of a soil contaminated by diuron using hydroxypropyl-β-cyclodextrin and organic amendments

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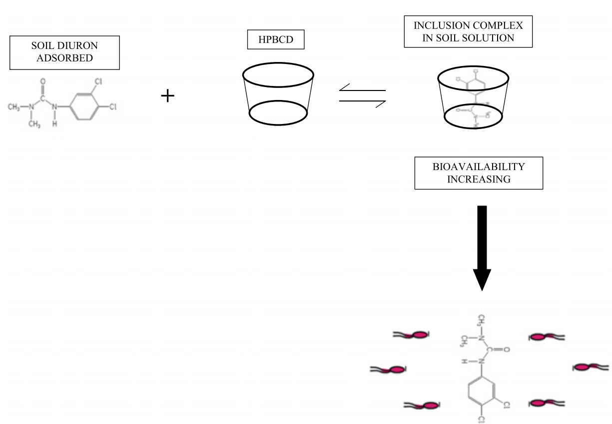
HIGHLIGHTS

- HPBCD acts as an enhancer for diuron bioavailability.
- Organic amendments (OAs) increase the rate of diuron mineralization.
- OAs supplied specific diuron degrading microorganisms.
- DOM from OAs acts as natural surfactant for diuron extraction.
- HPBCD plus OAs application causes a positive synergy on diuron rate mineralisation.

GRAPHICAL ABSTRACT



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ABSTRACT

Diuron desorption and mineralisation were studied on an amended and artificially contaminated soil. The amendments used comprised two different composted organic residues i.e., sewage sludge (SS) mixed with pruning wastes, and urban solid residues (USR), and two different solutions (with inorganic salts as the micronutrients and hydroxypropyl-β-cyclodextrin (HPBCD)). After applying micronutrients to activate the soil flora, 15.5% mineralisation could be reached after 150 days, indicating that the soil has a potential capacity to mineralise the herbicide through biostimulation-assisted attenuation. Diuron mineralisation was also improved when HPBCD solutions were applied. Indeed, the extent of herbicide mineralisation reached 29.7% with this application. Moreover, both the lag phase and the half-life time (DT_{50}) were reduced to 33 and 1778 days, respectively, relative to the application of just micronutrients (i.e., 39 and 6297 days, respectively). Organic amendments were also applied (i.e., USR and SS) on the contaminated soil: it was found that the diuron mineralisation rate was improved as the amendment concentration increased. The joint application of all treatments investigated at the best conditions tested was conducted to obtain the best diuron mineralisation results. The micronutrient amendment plus 4% USR or SS amendment plus HPBCD solution (10-fold diuron initially spiked) caused an extent of diuron mineralisation 33.2 or 46.5%, respectively.

1. Introduction

Phenylurea herbicides are widely used for the general control of non-crop areas and for selective pre- and post-emergence weed control on crops such as asparagus, cotton, maize or wheat; consequently, these

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Table 1
Main properties of the composts used.

Properties	USR	SS
Organic matter (%)	79	22
pH	6.7	6.4
Electrical conductivity (dS m^{-1})	8.7	8.0
N Kjeldahl (%)	1.8	1.7
P_2O_5 (%)	0.6	3.9
K_2O (%)	1.2	0.8
CaO (%)	5.4	9.5
MgO (%)	0.4	1.2
Na (%)	0.6	0.0
Fe (%)	0.5	1.9
Mn (mg kg^{-1})	86	252
Cu (mg kg^{-1})	57	325
Zn (mg kg^{-1})	49	563
Pb (mg kg^{-1})	60	184
Ni (mg kg^{-1})	16	59
Cd (mg kg^{-1})	<1	2.0
C/N ratio	44	13
Dissolved organic matter (g kg^{-1})	0.7	0.1
Microbial content (CFU g^{-1}). Specific diuron degraders	23×10^5	68×10^5
Soluble phosphorous (mg L^{-1})	90	17
Soluble nitrogen (mg L^{-1})	670	60×10^3

herbicides constitute important environmental pollutants. Diuron is one such herbicides and it is the one that is most frequently detected in groundwater (Di Bernardo et al., 2011; Giaccomazzi and Cochet, 2004). Moreover, this herbicide is included in the list of priority hazardous substances of the European Union (Malato et al., 2003), and is subjected to emission controls and quality standards to achieve "progressive reduction of discharges, emissions and losses".

Diuron attenuation in the environment is primarily achieved through microbial degradation processes (Villaverde et al., 2012). This mechanism yields the corresponding aniline derivatives, for example 3,4-dichloroaniline (DCA), which are considered to be more harmful to non-target organisms compared with the parent herbicide. Although there are numerous studies on diuron dissipation in soil–water systems, the complete diuron mineralisation has been described relatively rarely in the literature (Sorensen et al., 2008, 2013; Villaverde et al., 2012, 2013a; Bazot and Lebeau, 2009). Mineralisation studies using ^{14}C-ring-labelled diuron have demonstrated slow mineralisation rates, with half-life values up to 4000 days in different soils (Muhamad et al., 2013). At this time it is appropriate to provide the definition of bioavailability and an interesting definition is that supplied by Katayama et al. (2010): "The amount of chemical available to be taken up or utilised by an organism/organisms in a defined time and environment". The most significant interaction between soils and xenobiotics that affects bioavailability is sorption, followed by ageing and bound residue formation. The rate of uptake and subsequent degradation of chemicals by organisms is generally determined by the concentration of the chemicals in soil solution. It has been observed that the rate of desorption is proportional to the rate of the mineralisation of the organic chemical (Villaverde et al., 2012, 2013b; Zhu and Aitken, 2010; Dou et al., 2011; Sun et al., 2012). For these reasons, the present investigations are focused on the development of different strategies for increasing the diuron bioavailability and therefore, mineralisation rate in soil–water systems. One of the strategies is the use of cyclodextrins (CDs), which are cyclic organic compounds that are obtained through the enzymatic transformation of starch. These molecules posses a hydrophobic cavity and an exterior that is strongly hydrophilic. This peculiar structure allows organic molecules to be included in the cavity via non-covalent bonds to form inclusion complexes (Morillo et al., 2012). In previous studies, complexes between diuron and different CDs were successfully obtained in solution, where the most successful complexation parameters and the highest solubility increment were obtained for HPBCD (Villaverde et al., 2012). Equally, previous works have been published in this area by the authors, who used a HPBCD solution at a very low concentration (i.e., only 10 times the diuron equimolar concentration in soil) as a bioavailability enhancer. This approach has the effect of accelerating the passage of the diuron-desorbing fraction from the soil particle surface to the soil solution, thereby improving the accessibility of the endogenous microorganisms to the herbicide (Villaverde et al., 2012, 2013a,b). Similarly, Villaverde et al. showed for the first time in 2012 that a cyclodextrin-based bioremediation technology coupled with the application of a specific bacterial diuron degrader consortium (bioaugmentation) was able to achieve almost a complete mineralisation of diuron in a soil–water system.

The other strategy is the use of compost obtained from different residues for diuron soil remediation. Composts are rich sources of xenobiotics-degrading microorganisms, which can degrade pollutants to innocuous compounds through the process of mineralisation. However, the application of composts can also decrease the bioaccessibility of chemicals, sequestering pollutants within the organic matrix of the soil. Although recycling different organic wastes provides benefits from an environmental point of view, to date, the use of composts has not been widely applied as a method for bioremediation (Semple et al., 2001). The success or failure of a compost remediation strategy depends on a number of factors, the most important of which are the bioavailability and biodegradability of the pollutant. The use of HPBCD has been demonstrated, as noted above, to accelerate the mineralisation rate of persistent contaminants in water–soil systems, which has enhanced their bioavailability. Therefore, the main objective of the present work will be to test if the joint application of both strategies can improve the mineralisation of diuron. These results will contribute to the discussion of establishing a bioremediation technique as a practical choice based on chemical bioavailability.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Technical grade (98%) *diuron* [N-(3,4-dichlorophenyl)-N, Ndimethylurea] was provided by PRESMAR S.L. (Seville, Spain). Radiolabelled [ring-U-^{14}C]-diuron was purchased from the Institute of Isotopes (Budapest, Hungary) with specific activity of 36 mCi $mmol^{-1}$, chemical purity of 99.9% and radiochemical purity of 100%. The CD employed was hydroxypropyl-β-CD (HPBCD) from Cyclolab (Budapest, Hungary) and had a chemical purity of 97%.

2.1.2. Soil

A loamy sandy agricultural soil from southwestern Spain with a pH of 8.7, 0.66% of organic matter (OM), 0.03 g kg^{-1} of dissolved organic matter (DOM) and a particle size distribution of 74% sand, 16% silt, and 10% clay was selected for this study. The sample was taken from the horizon (0–20 cm), air-dried for 24 h, and sieved through 2 mm to remove stones and plant materials. The soil was frozen until its use. The soil was analysed for particle size distribution (as measured using a Bouyoucos densimeter), organic matter (as measured by $K_2Cr_2O_7$ oxidation), pH (determined in the 1:2.5 soil/water extract), and total carbonate content (as measured using the manometric method).

2.1.3. Amendments

The micronutrients (trace elements, TEs) $CaSO_4 \cdot 2H_2O$, $ZnSO_4 \cdot 7H_2O$, $Al_2(SO_4)_3 \cdot 16H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, KBr, KCl, $MnCl_2 \cdot 4H_2O$, $SnCl_2 \cdot 2H_2O$ and $FeSO_4 \cdot 7H_2O$ were used as the inorganic amendment (Fenlon et al., 2011) in the mineralisation experiments. Additionally, two composts were used as the organic amendments. The first, USR compost, was obtained from an experimental reactor that uses food residues at the University of Huelva (López et al., 2011). The second, a composted Biosolid (SS), was obtained from sewage sludge from a Wastewater Treatment Plant in Sevilla.