



Assessment of soil diuron bioavailability to plants and microorganisms through non-exhaustive chemical extractions of the herbicide



M. Rubio-Bellido, E. Morillo, J. Villaverde*

Instituto de Recursos Naturales y Agrobiología (IRNAS-CSIC), Apartado 1052, 41080 Sevilla, Spain

ARTICLE INFO

Handling Editor: Yvan Capowiez

Keywords:

Diuron
Bioavailability
Mild extractions
Contaminated soil
Bioremediation
Plant toxicity

ABSTRACT

In environmental and soil sciences, bioavailability represents the amount of an element or compound that is accessible to an organism for uptake or adsorption across its cellular membrane. In agricultural applications, almost exclusively plant roots and soil organisms uptake contaminants that are dissolved in the soil water. On this basis, a study was conducted to determine the relationship between diuron bioavailability to plants or microorganisms of aged herbicide residues in 10 selected soil types, and their extraction from these soils using three different solutions: *n*-butanol, hydroxypropyl- β -cyclodextrin (HPBCD) and CaCl_2 . The aim of the mineralisation bioassays was to assess the diuron bioavailable fraction mineralised by a diuron soil microbial degrader consortium. The bioassays using plants aimed to assess the diuron biotoxicity employing a selected crop (*Hordeum vulgare*). Toxicity was determined as the level at which plant growth was inhibited.

Aging of diuron contaminated soil during 100 days drastically decreased the percentage of diuron recovered by the selected extractants in all the tested soils. Results showed statistical correlations between non-exhaustive chemical diuron extraction and biological measurements when the extractant was *n*-butanol, showing to be the most reliable chemical technique capable of predicting both, diuron bioavailability for microorganisms and for plants. HPBCD was also capable of detecting diuron bioavailability only for microorganism, although with worse statistical data, while the third extractant, CaCl_2 aqueous solution, showed to be the least reliable for both assays. The results presented demonstrated that a non-exhaustive chemical extraction using *n*-butanol as extractant may serve as the basis for a simple and rapid procedure to assess diuron bioavailability in contaminated soils with different characteristics.

1. Introduction

After an organic hydrophobic pollutant arrives to the soil, this may be lost by biodegradation, leaching or volatilization, but it may also accumulate within the soil biota or be retained or sequestered within the soil's mineral and organic matter fractions. As the time of contact increases between soil and pollutant there is a decrease in chemical and biological availability, a process termed 'aging'. The availability of many chemicals in soils is affected by different processes. Organic contaminants generally exhibit two kinetic stages within the soil. Initially, a portion of the organic contaminant can be sorbed quickly (in minutes to a few hours), whereas the remaining fraction is sorbed more slowly over weeks or months (Xing and Pignatello, 1997). The initial rapid sorption is generally by hydrogen bonding and Van der Waals forces, mechanisms that are expected to occur instantaneously upon contact of the organic pollutant with the soil particles (Gevao et al., 2000). Two concepts have been proposed to describe the sequestration of the remaining fraction in soils: (i) diffusion through organic matter

and (ii) sorption-retarded pore diffusion (described in detail in Pignatello and Xing, 1996). Therefore, the extent and rate of microbial degradation of an organic compound and its metabolites is significantly controlled by its bioavailability, where a good definition could be "the fraction which is freely available to cross the organisms' cellular membrane from the medium the organism inhabits at a given time" (Semple et al., 2004). However, although a large amount of research effort has been expended on soil chemical bioavailability, there is neither a universally accepted definition on bioavailability nor standardised means of measuring it (Hodson et al., 2011). This is a reflection, in part, of the complexity of the soil system and the legislative requirements of the different countries. From the perspective of contaminated sites and their remediation, the concept of soil pollutant bioavailability would be key to assess what proportion of a contaminant and/or metabolites formed present at the contaminated site is available for uptake by organisms and is thus potentially able to cause harm. From this point of view, an emerging consensus appears to be that, bioavailability should be studied from a biological perspective, and

* Corresponding author.

E-mail address: j.villaverde@csic.es (J. Villaverde).

therefore, the predictive power could be grouped according to the objective of the bioavailability tests: whether for risk assessment (damage caused to the target organism) (Marziali et al., 2017) or remediation (pollutant biodegradation/mineralisation) (Villaverde et al., 2017). The simplest method of determining the pollutant soil bioavailable fraction would be to expose the target organism and measure the uptake of the pollutant into the organism. For instance, in the case of microorganism measuring the biological mineralisation rate in the presence of those capable to degrade a specific pollutant.

The concept of aging has been raised in sorption-desorption studies to explain the phenomenon of hysteresis or irreversibility of sorption and desorption. Aging may lead to decreased bioavailability and toxicity of organic pollutants and their metabolites via immobilization or sequestration. Reduced bioavailability of such a chemical is shown through the decline in the rate of biodegradation with time (aging) or by showing an almost complete resistance of the molecule to be biodegraded, called in this case as recalcitrant molecule or bound residue (Alexander, 2000). The bound residues of pesticides are defined as “chemical species originating from pesticides, used according to good agriculture practice, that are unextractable by methods which do not significantly change the chemical nature of the residue” (IUPAC). Northcott and Jones (2001) extended this definition to include that “the bound residues formation reduces the bioaccessibility and bioavailability significantly”. The term bound residues is reserved only for residues proven to be covalently bound to or irreversibly sequestered within the soil matrix, which is in general highly difficult to validate, and hence, the use of non-extractable residues (NER) is more appropriate (Kastner et al., 2014). The formation of pesticide NER during access and turnover in soil is generally considered to be based on various physical and chemical interactions between the parent xenobiotic or its xenobiotic metabolites and SOM, clay minerals, and organo-clay complexes.

Different physico-chemical extractions have been developed to predict the bioavailable fraction of pollutants in a soil. The most straightforward extractions involve shaking soil with a weakly polar (methanol-water, methanol, *n*-butanol, etc.) solvents or salt solutions with the aim of simulating soil solution (Villaverde et al., 2013). Some solubilising agents such as cyclodextrins (CDs) (Semple et al., 2013; Fenlon et al., 2011; Papadopoulos et al., 2007) and surfactants (Cuyper et al., 2002) have also been employed for bioavailability assessment of different organic pollutants in soil. Reid et al. (2004) proposed the use of a hydroxypropyl- β -cyclodextrin (HPBCD) solution to predict the soil bioavailable fraction of sorbed polycyclic aromatic hydrocarbons (PAHs). It is well-known that CDs are capable of forming inclusion complexes in solution with a variety of hydrophobic guest molecules, which could be placed in their hydrophobic interior cavity. Most pesticide – CD complexes were aimed to improve their solubility in water (Rubio-Bellido et al., 2016; Villaverde et al., 2004). Bioassays have been also used for the risk assessment of contaminated soils (Loibner et al., 2004). The success of bioassays has been observed when used in conjunction with a chemical procedure, correlating a non-exhaustive

extraction with biodegradation/mineralisation and toxicity assays to substantiate the predictive power of the chemical assay (ISO 17402:2011). The chemical assays which measure the dissolved and rapidly desorbing fraction, simulate availability to microorganisms (Alexander, 2000). However, the uptake mechanisms of higher organisms are more complex and could be more difficult to assess with a mild solvent extraction (Reid et al., 2000a).

Diuron has a low to moderate log Kow = 2.6, however, this compound has a soil-organic fraction partition constant (Koc) of 485, which predicts its adsorption affinity to soil organic particles. Diuron can be considered as a strongly adsorbed herbicide by soil organic matter particles and, hence, a recalcitrant chemical which is slowly degraded in the environment due to its reduced bioavailability. Phenylurea herbicides are biodegraded in soil both by biotic or abiotic degradation, and could lead to accumulation of very toxic metabolites, such as 3, 4-dichloroaniline. The most influential properties affecting the aging of organic residues are the total organic matter content in soils, when > 1%, and clay content in soils when lower than 1% in organic matter (Rubio-Bellido et al., 2016; Villaverde et al., 2008; Spark and Swift, 2002). The octanol–water partition coefficient (Kow) of the pesticide is also an indicator as to the likelihood of NER formation, with a higher Kow resulting in greater affinity for adsorption on soil particles and lower mobility (Morillo et al., 2004).

This paper aims to assess the risk of aged residues of the herbicide diuron in a contaminated soil from a toxicological and potential bioremediation point of view. For this purpose, two type of assays were raised: i) a non-exhaustive removal of sorbed diuron residues from ten soils with different properties, after aging for 100 days and extracted using *n*-butanol, cyclodextrin and calcium chloride solutions; and ii) two bioassays to assess the soil diuron bioavailable fraction, through measurements on toxicity effects on plant growth (using a target crop) and potential bioremediation of a diuron contaminated soil (using a soil degrader microbial consortium). The results obtained from both assays will be statistically correlated in order to determine which extractant is capable to make bioavailability predictions for diuron in soils.

2. Materials and methods

2.1. Materials

Technical grade (98%) diuron [*N*-(3,4-dichlorophenyl)-*N,N*-dimethylurea] was provided by Presmar S.L. (Seville, Spain). Radiolabelled [ring-¹⁴C]-diuron was purchased from Institute of Isotopes, Budapest, Hungary (specific activity = 36 mCi mmol⁻¹, chemical purity = 99.9%, and radiochemical purity = 100%). Hydroxypropyl- β -cyclodextrin (HPBCD) was purchased from Cyclolab, Budapest, Hungary. Ten different soils from Southwestern Spain were employed in this study. All soils were preserved by freezing until further usage. Soil analyses were performed as described by Rubio-Bellido et al. (2016). The soil specific surface area was determined in duplicate using the Brunauer Emmet Teller (BET) method. The adsorption of N₂

Table 1
Soil properties.

Soils	pH	CaCO ₃ (%)	OC (%)	Sand (%)	Silt (%)	Clay (%)	Textural classification	Average pore width (nm)
1	8.58	11.0	0.12	95.3	4.10	0.60	Sandy	4.03
2	8.68	11.6	0.38	73.9	16.1	10.0	Sandy loamy	5.02
3	8.73	27.5	1.02	59.4	15.9	24.6	Sandy loamy	4.12
4	6.00	0.00	0.82	16.7	58.6	24.7	Silt loamy	7.00
5	8.30	21.4	1.69	64.0	16.5	18.3	Sandy loamy	2.56
6	8.24	9.70	0.97	47.0	17.1	34.5	Clay loamy	5.02
7	8.00	24.1	1.02	2.70	31.5	65.9	Clay	3.44
8	5.50	0.00	0.91	49.8	34.5	15.7	Loamy	7.54
9	6.97	2.00	1.24	31.6	53.6	14.8	Silt loamy	7.18
10	6.23	1.60	1.96	24.2	59.4	16.4	Silt loamy	8.57

Download English Version:

<https://daneshyari.com/en/article/8894374>

Download Persian Version:

<https://daneshyari.com/article/8894374>

[Daneshyari.com](https://daneshyari.com)