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Pesticide metabolites as contaminants of groundwater resources: assessment of the leaching potential of endosulfan sulfate, 2,6-dichlorobenzoic acid, 3,4-dichloroaniline, 2,4-dichlorophenol and 4-chloro-2-methylphenol

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Abstract

This study reports the results of K_{oc} and soil DT_{50} experiments used for the definition of the leaching potential through the GUS Index of five metabolites: endosulfan sulphate (ES) from endosulfan, 2,6-dichlorobenzoic acid (DBA) from dichlobenil, 3,4-dichloroaniline (DCA) from propanil, 2,4-dichlorophenol (DCP) from 2,4-D and 4-chloro-2-methylphenol (CMP) from MCPA. The K_{oc} values for all the compounds were lower than 300, indicating high potential mobility in soil. Soil DT_{50} values were around 24 days for DBA and ES, and <3 days for the other three metabolites. The leaching potential expressed by the GUS Index was high for DBA and ES (>2.8) and low to negligible for CMP, DCA and DCP (<0.32). In short, the intrinsic characteristics of DBA and ES are typical of leachers, but their significance as groundwater contaminants should be further surveyed through leaching in soil columns treated with their parent compounds.

Keywords: Leaching potential; Pesticide metabolites; Degradation products; K_{oc}; DT_{50}; GUS

1. Introduction

Once in the environment, pesticides may be transformed into a large number of degradation products, commonly defined as metabolites. Many studies report the presence of pesticide metabolites in groundwater [1–12]. In spite of this, they are rarely included in monitoring programmes also for the difficulty to identify those of primary importance. Due considerations being given to this, an approach was developed by which over 60 metabolites have been selected, relevant to various categories of pesticides.

This approach consists of: (a) individuation of metabolites from parent compounds extensively used in agriculture; (b) evaluation of existing data on the environmental, toxicological and ecotoxicological properties of metabolites so as to preselect those to which priority should be attached; (c) assessment of the leaching potential of metabolites with known or unknown environmental properties by applying the Groundwater Ubiquity Score Index (GUS) [13], after having measured their K_{oc}, i.e. partition coefficient between soil organic carbon and water, and soil DT_{50}, i.e. soil degradation half-life of a compound, with quick, standardized laboratory tests; (d) confirmation of their leaching behaviour (GUS≥2.8) by means of soil leaching column experiments, which allow to assess their relevance as groundwater pollutants on the basis of the percentage of formation in leachates; (e) research into selected groundwater lying underneath agricultural areas where the corre-

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Table 1
Main characteristics of the soil used in the DT_{50} experiments

Pedological horizon	A	coarse sand (%)	26.4
Sample depth (cm)	5–15	fine sand (%)	15.1
Organic carbon (%)	1.4	silt (%)	47.0
pH (H_2O)	8	clay (%)	11.5
CEC (meq/100 g)	14.95	moisture content (w/w%)	22%
Water holding capacity max (%)	34%	texture classification (USDA)	F

sponding parent compounds are applied. This approach has been partly or fully applied in previous works in which several pesticide metabolites have been already examined for their potential to contaminate groundwater [14–17].

This study reports the results of K_{oc} and soil DT_{50} experiments used for the definition of the leaching potential through the GUS Index of the following metabolites: endosulfan sulphate (ES) from endosulfan, 2,6-dichlorobenzoic acid (DBA) from dichlobenil, 3,4-dichloroaniline (DCA) from propanil, 2,4-dichlorophenol (DCP) from 2,4-D and 4-chloro-2-methylphenol (CMP) from MCPA.

ES is the main product of the oxidative degradation in soil of the insecticide endosulfan. It degrades slowly in soil with respect to parent, and tends to accumulate in aquatic organisms and to be adsorbed in sediments, ES is also a main metabolite in plants and some mammals [18]. In insects and mammals, ES has the same toxicity of the parent compound [19]. It has been occasionally detected in groundwater (0.18 μg/l) [20].

DCA is formed in soil from the hydrolysis of propanil, catalyzed by soil microorganisms. A similar step was observed in plants, in rat liver microsomes and in mammals (in vivo) [18].

DCP is formed in soil from the oxidation of the side chain of the herbicide 2,4-D. It has been found in groundwater at levels up to 3.3 μg/l [21].

CMP is the main product of the oxidative degradation in soil of the herbicide MCPA [22]. No information seems to be available on its occurrence in the environment.

DBA is formed, in the environment, from the hydrolysis of the nitrile group of the parent herbicide dichlobenil and the subsequent hydroxylation at the three-position of the phenyl ring [18].

2. Experimental

2.1. Reagents

Pesticide metabolites were purchased from Dr. Ehrenstorfer (Augsburg, Germany) and their degree of purity was ≥96.5%. All the organic solvents (HPLC grade) were from commercially available sources (acetone Baker, Holland; methanol Sigma Aldrich, Germany; acetonitrile Merck, Germany). Distilled water for high performance liquid chromatography (HPLC) was further purified by using a Norganic cartridge (Millipore, Bedford, MA, USA).

2.2. Determination of soil DT_{50}

The degradation experiments were conducted on fresh soil, not previously treated with pesticides, which was collected in an agricultural field representative for corn production of the province of Bergamo (Lombardia Region, Italy). This soil type was usually employed in other degradation experiments conducted in our laboratory. The physical–chemical characteristics and texture of the soil are reported in Table 1. For each of the tested compounds, degradation experiments were performed on two soil replicates (each in duplicate), according to published procedures [15,16] and to the Guidelines of the Society of Environmental Toxicology and Chemistry [23]. The main experimental conditions and detection equipments are summarized in Table 2, further instrumental details are described elsewhere [16,17]. The doses of application were 10 mg/kg for ES and 5 mg/kg for the other substances in order to facilitate their analytical detection. All the compounds were extracted from soil with initial recoveries of 40% and 50% for DBA and ES, respectively, 70%, 80% and 98% for CMP, DCA and DCP, respectively. The recoveries for DBA and ES were rather low but sufficient for their detection within the whole period of the experiment. The HPLC mobile phase used for DCA was a mixture of acetonitrile (A) and water at the following percentages: from 0 to 5 min A is kept at 20%, from 5 to 20 min A linearly increases from 20% to 80%, from 20 to 25 min A remains at 80%, then linearly decreases to 20% from 25 to 30 min, and remains stable till 35 min. The HPLC conditions for the other compounds were acetonitrile–water 50:50, pH 2.55

Table 2
Experimental details related to the determination of soil DT_{50} and K_{oc}

SOIL DT_{50}		K_{oc}	
Incubation temperature	21 °C	analytical equipment	RP-HPLC/DAD
Length of each test	up to DT_{90}	wavelength (nm)	210
Reference compound	atrazine	column	Supelcosil LC-CN
Extraction solvent	CH_3CHO	mobile phase	CH_3OH/H_2O (55:45)
Analytical equipment	RP-HPLC/DAD	elution	isocratic
Wavelength (nm)	205–210	reference compounds:	
Column	25 cm length×Ø 4.6 mm, 5 μm particle size RP-amide C_{16}	acetanilide, atrazine, diclofop-methyl, isoproturon, linuron, methiocarb, phenol	
Flow rate	1 ml/min		
Mobile phase	CH_3CN/H_2O gradient see text		