Chemosphere 75 (2009) 100–108

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Sorption characteristics of pesticides on matrix substrates used in biopurification systems

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ARTICLE INFO

Article history:
Received 13 June 2008
Received in revised form 31 October 2008
Accepted 16 November 2008
Available online 21 December 2008

Keywords:
Pesticide
Sorption isotherm
Freundlich isotherm
Competitive sorption
Matrix substrate

ABSTRACT

On-farm biopurification systems were developed to remove pesticides from contaminated water generated at the farmyard. An important process in the system's efficiency is the sorption of pesticides to the substrates used in the biopurification systems. The composition and type of material present in the biobed are crucial for retention of chemicals. This study investigated the sorption of linuron, isoproturon, metalaxyl, isoxaben, bentazon and lenacil on substrates commonly used in a biopurification system, i.e. cow manure, straw, willow chopping, soil, coconut chips, garden waste compost, and peat mix. Linear, Freundlich, and Langmuir sorption isotherms were fitted to the obtained data. The best fit was obtained with the Freundlich model. More immobile pesticides (i.e. linuron and isoxaben) tended to associate with the organic substrate, while more mobile pesticides partition in the water (i.e. bentazon). According to sorption capacity, the substrates could be classified as peat mix > compost, coco chips, straw > cow manure, willow chopping > sandy loam soil. Sorption capacity was positively correlated with the organic carbon content, CaO and the cation exchange capacity. Furthermore, no significant differences in sorption could be found between technical and formulated isoproturon and bentazon. Moreover, the individual sorption coefficient K_d was additive, which means that individual sorption coefficients can be used to calculate the sorption coefficients of a mixture of substrates. What concerns the mutual interaction of pesticides it could be observed that the sorption of linuron and metalaxyl was significantly lower in combination with isoproturon and bentazon, while the latter pesticides were not influenced by the presence of linuron and metalaxyl. As guidelines, firstly, it could be stated that using the most sorbing materials such as peat mix, might significantly increase the biopurification systems efficiency. Secondly, the treatment of very mobile pesticides, such as bentazon, should be taken with care as these will easily leach through the system. Additional chemical treatment might be necessary for these type of pesticides.

1. Introduction

Contamination of water bodies with agricultural pesticides poses a significant threat to aquatic ecosystems and drinking water resources (Dabrowski and Schulz, 2003). Emissions of pesticides in the environment are generally divided into diffuse and direct losses. Diffuse contamination via percolation, runoff, drainage and drift explains only a part of the pesticides that reach surface and groundwater. Several field surveys and measurement campaigns demonstrated that 40–90% of surface water contamination is attributable to direct losses (Mason et al., 1999; Carter, 2000; Kreuger and Nilsson, 2001; Decoin, 2003; Jaeken and Debaer, 2005). The main direct losses are caused by spillages during the filling and cleaning of the spraying equipment and leakages of the spraying equipment, etc. (Isensee and Sadeghi, 1996; Shepherd and Heather, 1999; Torstensson and Castillo, 1997; Ramwell et al., 2004). Several techniques have been developed for the removal of pesticides from water. Sorption on activated carbon is the most widespread technology used to deal with purification of water contaminated by pesticides and other hazardous chemicals (Baup et al., 2000; Heijman and Hopman, 1999). However, due to high cost of activated carbon, its use in the field is sometimes restricted due to economical considerations. Moreover, the high cost associated with its regeneration led to explore new inexpensive materials (Gupta et al., 2006). For the last decades, sorption of contaminants by sorbents of natural origin has gained important credibility due to the good performance and low cost of these complex materials (Bras et al., 1999; Chubar et al., 2003; Sheng et al., 2005; Yang and Sheng, 2003a,b).

A technique which uses natural materials (agricultural waste products or products available on-farm) to create a pesticide retaining and degrading environment to clean contaminated water

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doi:10.1016/j.chemosphere.2008.11.037

on-farm, has been developed in Sweden (Torstensson and Castillo, 1997; Torstensson, 2000) and was called a biobed. Variations to this system have been developed in the UK, France, Belgium, Italy and are also called Phytobac® and biofilter. The concept of these three systems is similar. They all consist of a biological active matrix that retains pesticides onto organic matter and soil particles, where enhanced or rapid microbial degradation of the pesticides occurs. The first reported substrate mix, also called "biomix", used in biopurification systems consisted of peat, straw and topsoil (Torstensson and Castillo, 1996), mixed in volumetric proportions of 1:2:1. The composition and type of organic material present in the biobed are believed to be crucial for retention of chemicals as well as for the amount and activity of microorganisms responsible for degradation of the pesticides (Castillo and Torstensson, 2007). Matrix substrates that can be used in a biopurification system can have differing organic carbon contents and more importantly, differing pesticide sorption capacities. In order to optimize and model the fate and transport of pesticides in the biopurification systems, sorption of the pesticides on the substrates should be profoundly characterized.

The partitioning of the pesticides between the solid and solution phase into the biological active matrix due to sorption process, depends on the physico-chemical characteristics of the surface. Although sorption on different types of soil has been characterized for a wide variety of pesticides, data are missing on the sorption of pesticides on organic materials such as compost, peat and straw used in on-farm biopurification systems. These data are essential to model the transport of pesticides in biopurification systems. The transport of the pesticide in water in the system will be influenced by degradation and retention and can be described with the convection dispersion equation. In order to accurately describe this equation, it is necessary to determine as much parameters (retention and degradation parameters) as possible. This model could than be used to predict the behavior of pesticides in the system and could identify problem pesticides which will be difficult to treat. Therefore the aim of this study was to investigate sorption of pesticides with varying physico-chemical characteristics on substrates already used in biopurification systems such as peat, soil and straw. Additionally, sorption on alternative substrates which are locally available or cheap such as compost, coco chips, willow chopping and cow manure were studied.

2. Materials and methods

2.1. Pesticide selection

The studied pesticides were selected based on their physico-chemical characteristics, degradability by micro organisms, and their frequency of detection in surface and groundwater and frequency of use. Pesticides were divided into four categories based on their persistence (*DT50* value) and mobility (K_{oc}) as described by De Wilde et al. (2007). This leads to the classification of pesticides into four categories: persistent-immobile, persistent-mobile, non-persistent-mobile and non-persistent-immobile. Selected pesticides of the non-persistent-mobile category were metalaxyl ($K_{oc} = 47$, $DT50_{soil} = 42$ days), bentazon ($K_{oc} = 13$, $DT50_{soil} = 14$ days) and isoproturon ($K_{oc} = 36$, $DT50_{soil} = 22.5$ days). As a non-persistent-immobile pesticide linuron was selected ($K_{oc} = 410$, $DT50_{soil} = 47.5$ days). While lenacil ($K_{oc} = 34$, $DT50_{soil} = 179$ days) and isoxaben ($K_{oc} = 862$, $DT50_{soil} = 262$ days) were selected as persistent-mobile and persistent-immobile pesticides, respectively.

2.2. Chemicals

Metalaxyl, isoproturon, linuron, lenacil, bentazon and isoxaben of analytical standard grade (99%) were purchased from Riedel-de Haen, Seelze, Germany. Technical grade metalaxyl (95.5% purity) was kindly supplied by Syngenta (Basel, Switzerland). Isoproturon, linuron, isoxaben, bentazon and lenacil were, respectively, used under the formulations Isoguard 83 WG (83% isoproturon, Gharda Chemicals Ltd., Surrey, England), Afalon SC (450 g L^{-1} linuron, Makhteshim Agan Holland B.V., Ieper, Belgium), AZ 500 (500 g L^{-1} isoxaben, Dow Agro Science, Wilrijk, Belgium), Basagran SG (87% bentazon, BASF, Antwerpen, Belgium) and Lenacil Protex 500 SC (500 g L^{-1} lenacil, Protex, Deurne, Belgium). Methanol, acetonitrile, water were of A.R. grade (VWR, Leuven, Belgium).

Formulated pesticides were dissolved in a 0.01 M solution of calcium chloride ($CaCl_2$) (Merck, Darmstadt, Germany) and 200 mg L^{-1} sodium azide (NaN_3) (Sigma–Aldrich, St. Louis, MO, USA) in distilled water. $CaCl_2$ was used as a background electrolyte to make phase separation easier and to simulate an ionic strength similar to that of a natural soil solution (Monkiedje and Spiteller, 2002), while NaN_3 was added to minimize biological activity. The aqueous pesticide solutions were prepared as concentrations of 1, 10, 1000, 2500 and 5000 mg L^{-1}. This range was based on the concentrations applied in the field. A high concentration could simulate a spill during filling, while low concentrations represented diluted waste water from cleaning the spraying equipment.

2.3. Substrate selection

The selected substrates were peat mix, garden waste compost, straw, sandy loam soil, cow manure, coco chips and willow chopping. These substrates have been discussed in detail in De Wilde et al. (2007). The main physico-chemical properties of these substrates are shown in Table 1. The soil used was a sandy loam soil with a texture of 33% sand, 56% loam and 11% clay and was air dried and crushed to pass a 2 mm sieve.

2.4. Sorption studies

Pesticide sorption on the substrates was studied using a batch equilibrium technique based on the OECD guideline 106 (Organization for Economic Co-operation and Development, 2000). For the

Table 1
Physico-chemical characteristics of the substrates used.

	pH	OC (g kg^{-1})	P_2O_5 (gk g^{-1})	K_2O (gk g^{-1})	CaO (gk g^{-1})	MgO (g kg^{-1})	Na (mg 100 g^{-1})	CEC (meq 100 g^{-1})	Specific density (mg m^{-3})
Garden waste compost	7.7	278.4	3.1	6.2	15.7	4.0	ND	ND	1.84
Willow chopping	5	427.6	9.3	36.4	29.4	7.8	0.26	28.44	1.57
Straw	6.6	423.6	6.9	77.2	3.8	3.6	0.57	25.21	1.56
Coco chips	6.7	446.9	9.8	123.9	0.8	1.0	2.52	58.98	1.67
Peat mix	6.4	476.1	4.5	8.0	670.0	7.9	0.42	129.42	1.58
Sandy loam soil	6.9	9.1	0.3	4.2	1.9	0.8	0.21	13.87	2.81
Cow manure	6.9	375.9	98.7	113.7	18.0	49.2	1.41	53.22	1.68

ND = not determined.