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Removal of carbofuran is not affected by co-application of chlorpyrifos in a coconut fiber/compost based biomixture after aging or pre-exposure

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ABSTRACT

Biomixtures constitute the biologically active part of biopurification systems (BPS), which are used to treat pesticide-containing wastewater. The aim of this work was to determine whether co-application of chlorpyrifos (CLP) affects the removal of carbofuran (CFN) (both insecticide/nematicides) in a coconut fiber–compost–soil biomixture (FCS biomixture), after aging or previous exposure to CFN. Removal of CFN and two of its transformation products (3-hydroxycarbofuran and 3-ketocarbofuran) was enhanced in pre-exposed biomixtures in comparison to aged biomixtures. The co-application of CLP did not affect CFN removal, which suggests that CLP does not inhibit microbial populations in charge of CFN transformation. Contrary to the removal behavior, mineralization of radiolabeled ^{14}C-pesticides showed higher mineralization rates of CFN in aged biomixtures (with respect to freshly prepared or pre-exposed biomixtures). In the case of CLP, mineralization was favored in freshly prepared biomixtures, which could be ascribed to high sorption during aging and microbial inhibition by CFN in pre-exposure. Regardless of removal and mineralization results, toxicological assays revealed a steep decrease in the acute toxicity of the matrix on the microcrustacean *Daphnia magna* (over 97%) after 8 days of treatment of individual pesticides or the mixture CFN/CLP. Results suggest that FCS biomixtures are suitable to be used in BPS for the treatment of wastewater in fields where both pesticides are employed.

Introduction

Biopurification systems (BPS) are biological devices developed as a tool to treat pesticide contaminated wastewater produced during agricultural activities (Karanasios et al., 2012). Use of BPS is mainly focused on reducing point source contamination such as accidental spillages during tank filling or mishandling of application residues or cleaning of spraying equipment, where the pesticide concentrations are usually high. BPS employ a biologically active biomixture where pesticides are removed from the wastewater by sorption and/or biodegradation. The biomixture acts as a filter matrix that will receive wastewater of high pesticide concentration during operation (initial operation concentrations in the order of mg/kg in the biomixture). This matrix is constituted by (Castillo et al., 2008): soil (usually pre-exposed to the target pesticide) that provides degrading microbiota, peat (as a humic component) and a lignocellulosic substrate (to promote the growth and activity of ligninolytic fungi, able to nonspecifically oxidize diverse organic pollutants, Asgher et al., 2008). Though peat has been usually employed in

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the first developed biomixture compositions, it has been successfully substituted by compost (Coppola et al., 2007; Kravvariti et al., 2010), which is more easily available at most geographical regions. Similarly, the use of lignocellulosic substrates has varied according to local availability, resulting in the use of alternative wastes such as cane bagasse, wood chips, olive leaves, grape stalks and barley husk (Karanasios et al., 2010; Urrutia et al., 2013; Chin-Pampillo et al., 2015a).

Efficiency of biomixtures is affected by diverse factors including moisture, temperature, composition, pre-exposure and maturity of the biomixture (Castillo et al., 2008). Among these factors, maturity, aging or pre-exposure of the biomixture have been scarcely studied. In this sense, Tortella et al. (2012) described the degradation of CLP at two maturity stages (15 and 30 days) and compared it to the un-aged biomixture, finding removal efficiencies over 50% in every case, however, the accumulation of the transformation product trichloropyridinol (TCP) was higher in the biomixture aged for 30 days. On the other hand, pesticide pre-exposure of the soil employed is suggested before preparation of biomixtures (Sniegowski et al., 2012), nonetheless few studies deal with the effect of the pre-exposure of the whole biomixture already prepared and usually report the outcome after successive pesticide applications (Vischetti et al., 2008; Tortella et al., 2013a, 2013b).

Carbofuran (CFN) is an insecticide that belongs to the group of carbamates, which also presents nematicide and acaricide activities, and poses a threat on non-target organisms due to its high toxicity (EC_{50} 0.0094 mg/L, acute test on *Daphnia magna*, 48 hr) (University of Hertfordshire, 2013), as it has been demonstrated by the occurrence of diverse alterations in aquatic life (Gupta, 1994; Adhikari et al., 2004). This pesticide is currently banned in the EU and the USA, and progressively in other latitudes, however, its use is still permitted in some countries, even though the banning in most of them is a matter of time; therefore while in use, measures to avoid contamination with CFN should be applied. Chlorpyrifos (CLP) is an organophosphate insecticide of worldwide use with a broad spectrum of activity. CLP is considered as a hydrophobic compound ($\log K_{ow} = 4.7$), with low water solubility (1.4 mg/L) and high affinity to organic matter ($K_{oc} = 8.5$ L/g), reasons why it shows strong adsorption and reduced bioavailability in soil (Racke, 1993; Racke et al., 1996), in contrast with CFN (K_{oc} = 0.086 L/g, $1/n = 0.89$) (University of Hertfordshire, 2013). The neurotoxic potential of CLP (EC_{50} 0.0001 mg/L, acute test on *D. magna*, 48 hr) (University of Hertfordshire, 2013) has been reviewed somewhere else (van Wijngaarden et al., 1993; Richardson, 1995; Eaton et al., 2008), and includes deleterious effects on aquatic life. The decrease in microbial abundance and activity has been observed in soil after contamination with CLP, which is usually ascribed to the production of TCP as a result of CLP hydrolysis; this process is considered to result in inhibition of CLP degradation (Racke et al., 1988; Chu et al., 2008). CFN and CLP can be applied to the same crops in tropical regions where CFN is still employed. Given the toxic effect of CLP on microbial communities, degradation of CFN could be affected in co-application of both compounds or in application of CLP in combination with other pesticides such as other carbamates.

The current study aimed to determine the effect of maturity and pre-exposure of a coconut fiber–compost–soil (FCS) biomixture on CFN degradation and mineralization, during single pesticide application and co-application of CLP. This FCS biomixture has been selected among several biomixtures due to its great efficiency to remove CFN (Chin-Pampillo et al., 2015a, 2015b). Additional toxicological assays yielded useful information on the feasible co-application of CFN and CLP into a single biomixture and the potential use of this matrix at environmental level.

1. Materials and methods

1.1. Chemicals and reagents

Commercial formulations of CFN (Furadan®48SC, 48%, *W/V*) and CLP (Solver®48EC, 48%, *W/V*) were acquired from a local store. Analytical standards CFN (2,2-dimethyl-2,3-dihydro-1-benzofuran-7-yl methylcarbamate, >99% purity), 3-hydroxycarbofuran (99.5%) and 3-ketocarbofuran (99.5%) were obtained from Chemservice (West Chester, Pennsylvania, USA). Radio-labeled CFN (^{14}C-CFN; [Ring-U-^{14}C]-Carbofuran; 2.89×10^9 Bq/g; radiochemical purity 100%; chemical purity 99.5%) and radio-labeled CLP (^{14}C-CLP; [Ring-2,6-$^{14}C_2$]-chlorpyrifos; 4.38×10^9 Bq/g; radiochemical purity 98.99%; chemical purity 98.34%) were obtained from Izotop (Institute of Isotopes Co., Budapest, Hungary). Carbendazim-d_4 (surrogate standard, 99.0%) and carbofuran-d_3 (internal standard, 99.5%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Potassium hydroxide analytical grade was purchased from Merck (Darmstadt, Germany). Ultima Gold cocktail for Liquid Scintillation Counting was purchased from Perkin Elmer (Waltham, Massachusetts, USA). Solvents and extraction chemicals are listed in Ruíz-Hidalgo et al. (2014).

1.2. Biomixture components and preparation

Clay loam soil (S) (sand 40%, silt 27%, clay 33%) was collected from the upper soil layer (0–20 cm) of an onion field with history of CFN application, in Tierra Blanca, Cartago, Costa Rica. Soil was air-dried and sieved through a 2-mm sieve. Coconut fiber (F) was acquired in a local market and garden compost (C) was collected from a composting station located at Universidad de Costa Rica and sieved as described for the soil after air-drying.

Biomixture was prepared by mixing coconut fiber, compost, and pre-exposed soil at a volumetric proportion of 50:25:25 and moistened to approximately 75% of maximum water-holding capacity (maximum water-holding capacity: 0.77 mL water/g biomixture). The biomixture was separated into three batches and treated as follows: FCS-fresh was used fresh prepared; FCS-pre was pre-exposed to CFN by spiking 25 mg/kg CFN and stored for 10 days (for CFN removal); and FCS-age was stored at 25°C during one month prior to use. In indicated experiments a biomixture pre-exposed and aged for five weeks was also employed (FCS-pre/age).

1.3. Experimental procedures

1.3.1. Degradation experiments

The degradation of CFN and the formation of its transformation products, 3-hydroxycarbofuran and 3-ketocarbofuran