Chemosphere 169 (2017) 558–567

Contents lists available at ScienceDirect

Chemosphere

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

Simultaneous removal of structurally different pesticides in a biomixture: Detoxification and effect of oxytetracycline

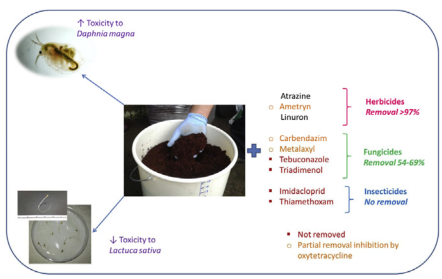
Alejandra Huete-Soto, Mario Masís-Mora, Verónica Lizano-Fallas, Juan Salvador Chin-Pampillo, Elizabeth Carazo-Rojas, Carlos E. Rodríguez-Rodríguez*

Centro de Investigación en Contaminación Ambiental (CICA), Universidad de Costa Rica, 2060 San José, Costa Rica

HIGHLIGHTS

- Removal of structurally diverse pesticides was simultaneously assayed in biomixtures.
- Herbicides and some fungicides were mostly removed after 70 d (optimum period).
- Neonicotinoid insecticides and triazole fungicides were not significantly removed.
- Co-application of oxytetracycline affected only removal of carbendazim and metalaxyl.
- Ecotoxicity towards *Daphnia magna* was not reduced but phytotoxicity decreased.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 July 2016
Received in revised form
28 October 2016
Accepted 20 November 2016

Handling Editor: A Adalberto Noyola

Keywords:
Antibiotics
Biopurification system
Degradation
Pesticides
Toxicity

ABSTRACT

The biopurification systems (BPS) used for the treatment of pesticide-containing wastewater must present a versatile degrading ability, in order to remove different active ingredients according to the crop protection programs. This work aimed to assay the simultaneous removal of several pesticides (combinations of herbicides/insecticides/fungicides, or insecticides/fungicides) in a biomixture used in a BPS over a period of 115 d, and in the presence of oxytetracycline (OTC), an antibiotic of agricultural use that could be present in wastewater from agricultural pesticide application practices. The biomixture was able to mostly remove the herbicides during the treatment (removal rates: atrazine ≈ linuron > ametryn), and suffered no inhibition by OTC (only slightly for ametryn). Two fungicides (carbendazim and metalaxyl) were removed, nonetheless, in the systems containing only fungicides and insecticides, a clear increase in their half-lives was obtained in the treatments containing OTC. The neonicotinoid insecticides (imidacloprid and thiamethoxam) and the triazole fungicides (tebuconazole and triadimenol) were not significantly eliminated in the biomixture. Globally, the total removal of active ingredients ranged from 40.9% to 61.2% depending on the system, following the pattern: herbicides > fungicides > insecticides. The ecotoxicological analysis of the process revealed no detoxification towards the microcrustacean *Daphnia magna*, but a significant decay in the phytotoxicity towards *Lactuca sativa* in some cases, according to seed germination tests; in this case, OTC proved to be partially responsible for the phytotoxicity. The patterns of pesticide removal and detoxification provide inputs for the improvement of BPS

* Corresponding author.
E-mail address: carlos.rodriguezrodriguez@ucr.ac.cr (C.E. Rodríguez-Rodríguez).

http://dx.doi.org/10.1016/j.chemosphere.2016.11.106

use and their relevance as devices for wastewater treatment according to specific pesticide application programs.

1. Introduction

In general, pest management in agriculture mainly includes the use of pesticides. Given their associated toxicity to non-target organisms, the pesticides may pose a threat in different ecosystems. In particular, occurrence of pesticides in the environment may be related to diffuse or point source contamination (Karanasios et al., 2012). The latter includes the contamination derived from leakages or improper handling of pesticide application equipment and the incorrect disposal of pesticide residues or equipment washing waters (De Wilde et al., 2007).

Biopurification systems (BPS) represent a biotechnological approach for the detoxification of pesticides present in wastewater produced in agricultural activities, and therefore their goal is the treatment of point sources of contamination (Castillo et al., 2008). Removal of pesticide residues is expected to occur faster in BPS than in soil, thanks to the presence of the biomixture, the biologically active component of BPS. The biomixture is composed of three materials: a lignocellulosic substrate, employed to enhance the colonization and activity of ligninolytic fungi, widely described as capable to transform organic pollutants (Yang et al., 2013), including pesticides (Mir-Tutusaus et al., 2014; Rodríguez-Rodríguez et al., 2013); soil, commonly pre-exposed to the target pesticides, which provides an adapted microbial community (Sniegowski et al., 2012); and finally a humic-rich component to enhance the retention of the pesticides in the matrix (Karanasios et al., 2012).

Agrochemicals employed for pest control also include antibiotics (Vidaver, 2002), often applied on crops in the same manner as pesticides. Therefore, antibiotic-containing wastewaters are also produced in agricultural activities and they could be potentially disposed in BPS. However, antibiotics could negatively affect the degrading capacity of the biomixture through the inhibition of some microbial populations, as these compounds may alter several microbial-mediated processes in the environment such as the degradation of organic matter and key reactions in the biogeochemical cycles of N and S (Kümmerer, 2009).

Taking into account that pesticide application programs include the use of several pesticides through the crop production cycle (according to diverse approaches of pest removal), it is desirable for the biomixtures to express a versatile degrading capacity to remove different active ingredients. This work aimed to evaluate the removal capacity of a biomixture during the simultaneous application of different pesticides (herbicides, fungicides and insecticides). The effect of oxytetracycline, an antibiotic of agricultural use, was assayed in the biomixture performance at a relevant BPS concentration. Ecotoxicological assays (acute toxicity on *Daphnia magna* and seed germination tests) were also conducted in order to better estimate the potential detoxification that takes place during the treatment process. The work yields relevant information on the application scope and design of biomixtures.

2. Materials and methods

2.1. Chemicals and reagents

Analytical standards atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine), ametryn (2-(ethylamino)-4-(isopropylamino-6-(methylthio)-1,3,5-triazine)), linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea), metalaxyl (methyl *N*-(methoxyacetyl)-*N*-(2,6-xylyl)-DL-alaninate), carbendazim (methyl benzimidazol-2-ylcarbamate), tebuconazole ((RS)-1-*p*-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)pentan-3-ol), triadimenol ((1RS,2RS;1RS,2SR)-1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol), imidacloprid ((E)-1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine) and thiamethoxam ((EZ)-3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene(nitro)amine) were obtained from Chem Service Inc. (West Chester, Pennsylvania, USA). Commercial formulations of atrazine (Atranex®, 90% w/w), ametryn (Agromart®, 50% w/v), linuron (Afalon®, 45% w/v), carbendazim (Agromart®, 50% w/v), metalaxyl (Abak®, 24% w/v), tebuconazole/triadimenol 3:1 (Silvacur® Combi 30 EC, 22.5% and 7.5% w/v, respectively), imidacloprid (Manager®, 35% w/v), thiamethoxam (Engeo®, 24.7% w/v) and OTC ((4S,4aR,5S,5aR,6S,12aS)-4-(dimethylamino)-3,5,6,10,11,12a-hexahydroxy-6-methyl-,12-dioxo-1,4,4a,5,5a,6,12,12a-octahydrotetracene-2-carboxamide; Terramicina Agrícola®, 5% w/w) were acquired from a local store. Carbofuran-d_3 (surrogate standard, 99.5%) and linuron-d_6 (internal standard, 98.5%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Solvents and extraction chemicals are listed in Ruiz-Hidalgo et al. (2014).

2.2. Experimental set-up

The removal of pesticides was assayed in a biomixture containing coconut fiber, compost and soil pre-exposed to carbofuran at a volumetric composition of 45: 13: 42, respectively (pH 6.4; C 4.83%; N 0.32%; C/N 15.2; P 0.22%; Ca 0.48%; Mg 0.71%; K 0.19%; S 0.07%; Fe 31 192 mg kg^{-1}; Cu 94 mg kg^{-1}; Zn 91 mg kg^{-1}; Mn 521 mg kg^{-1}; B 66 mg kg^{-1}; EC 0.6 mS cm^{-1}). The biomixture composition was previously optimized in order to maximize the removal of carbofuran and to reduce the residual toxicity of the matrix (Chin-Pampillo et al., 2015). The removal assays were performed in buckets (14 cm radius, 29 cm height) containing 10 L (~7.7 kg) of the biomixture. Four buckets were prepared; one (M) was spiked with a mixture of the commercial formulations of herbicides (atrazine, ametryn and linuron), fungicides (carbendazim, metalaxyl, tebuconazole and triadimenol) and insecticides (imidacloprid and thiamethoxam), to give a final nominal concentration of 25 mg kg^{-1} each (except triadimenol, 8.3 mg kg^{-1} which is contained in the same formulation of tebuconazole at a lower concentration). The second bucket was prepared using the same pesticide mixture and concentrations, plus Terramicina Agrícola 5WP® added at a final concentration of OTC of 17 mg kg^{-1} (M + O). A third bucket was spiked with the mixture of insecticides and fungicides (IF), while the forth contained the insecticides, fungicides and OTC (IF + O). All of the buckets were incubated in static conditions at 25 °C until the end of the assay; water was added when necessary in order to keep constant water content in the matrix.

Duplicate biomixture samples were periodically withdrawn from every single system during a period of 115 d to determine the concentration of pesticides (5 g), and to perform ecotoxicological