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Effects of oxytetracycline on the performance and activity of biomixtures: Removal of herbicides and mineralization of chlorpyrifos

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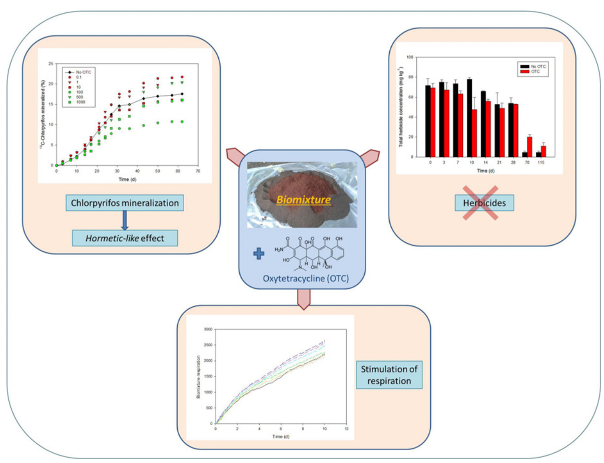
HIGHLIGHTS

- Effect of oxytetracycline (OTC) on pesticide removal was assayed in a biomixture.
- Biomixture respiration was mostly stimulated with the application of OTC.
- Chlorpyrifos mineralization improved at low OTC doses, resembling a hormetic effect.
- The biomixture was able to remove three herbicides simultaneously.
- During herbicide removal, OTC co-application only increased the half-life of ametryn.

GRAPHICAL ABSTRACT



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ABSTRACT

Biopurification systems (BPS) are design to remove pesticides from agricultural wastewater. This work assays for the first time the potential effect of an antibiotic of agricultural use (oxytetracycline, OTC) on the performance of a biomixture (biologically active core of BPS), considering that antibiotic-containing wastewaters are also produced in agricultural labors. The respiration of the biomixture was stimulated in the presence of increasing doses of OTC ($\geq$100 mg kg^{-1}), and only slightly increased with lower doses ($\leq$10 mg kg^{-1}). When co-applied during the removal of chlorpyrifos, OTC increased chlorpyrifos mineralization rates at low doses, resembling a hormetic effect. The biomixture was also able to remove three herbicides (atrazine, ametryn and linuron) with half-lives of 24.3 d, 43.9 d and 30.7 d; during co-application of OTC at a biomixture-relevant concentration, only the removal of ametryn was significantly inhibited, increasing its half-life to 92.4 d. Ecotoxicological assays revealed that detoxification takes place

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in the biomixture during the removal of herbicides in the presence of OTC. Overall results suggest that co-application of OTC in a biomixture does not negatively affect the performance of the matrix in every case; moreover, the co-application of this antibiotic could improve the mineralization of some pesticides.

1. Introduction

Biopurification systems (BPS) appeared as a biotechnological strategy to reduce the point source contamination generated from the application of pesticides in the agricultural industry. BPS are intended to rapidly degrade the pesticides contained in the wastewater produced during the filling, application and washing of pesticide application equipment in the field [1,2]. They contain a biomixture composed of a lignocellulosic substrate, a humic material, and soil, which is in charge of the retention and biodegradation of the pesticides. Most of the degrading microbial communities are provided by the soil, and therefore it should be preferably pre-exposed to the target pesticides; the lignocellulosic substrate promotes the colonization of ligninolytic fungi, which are linked to the unspecific oxidation of organic contaminants [3], including pesticides and other agrochemicals [4,5]; and the humic component (usually peat or compost) favors the retention of the pesticides and provides degrading microbiota [2].

Among pesticides, the herbicides are employed to control undesirable weeds; they are considered as the most widely employed pesticides worldwide due to the amounts used and the areas treated [6]. Atrazine and ametryn are herbicides of the chemical group of the triazines, and the former is the most extensively used member of this family [7]. Though they are not approved for use in the EU, their extensive application elsewhere for the control of broadleaf weeds in crops such as corn and sugarcane, makes their fate in the environment a matter of concern. Ametryn is considered as moderately soluble and persistent in water, and persistent in soil. Comparatively, atrazine presents lower water solubility and is less persistent in soil and water; moreover, atrazine presents higher risk of leaching to groundwater than ametryn. In terms of ecotoxicological risk, both herbicides show moderate toxicity to mammals, aquatic life, honeybees and earthworms [8]. Linuron is an herbicide that belongs to the phenylurea group, widely employed to control annual and perennial broadleaf and grassy weeds in diverse crops such as citrus fruits, bananas, corn and potato [8]. It is slightly soluble in water and potentially persistent, moderately mobile and semi-volatile in the environment [9]. Linuron is moderately toxic for aquatic life [8], affects mitochondrial activity of rats, shows low acute toxicity for humans, and is classified as a carcinogen [9].

Chlorpyrifos is an organophosphate insecticide and acaricide of broad application worldwide; it exhibits low water solubility and high affinity to organic matter, which results in low risk of leaching to groundwater. This pesticide is known to show high toxicity not only towards aquatic life, but also towards honeybees, birds and mammals; for the latter, chlorpyrifos is classified as a reproduction toxicant, an acetylcholinesterase inhibitor and a neurotoxicant [8].

However, the use of agrochemicals in agricultural activities is not circumscribed to pesticides. In this respect, some antibiotics have been employed in the control of diverse plant diseases that affect crops of agricultural importance since the 1950s. Nowadays, scarce antibiotics are used in agriculture; only oxytetracycline (OTC), streptomycin and gentamicin are currently registered by EPA for this use [10]; nonetheless other antibiotics such as kasugamycin, oxolinic acid and validamycin are used in many regions worldwide. Due to the adverse effects of antibiotics over selected microbial communities, several processes that naturally take place in the environment can be potentially affected or inhibited by their presence in the ecosystems. Such processes include the degradation of organic matter in soil and sewage systems, anaerobic digestion, nitrification and sulfate reduction [11]. The spread of microbial resistance to antibiotics due to their presence in the environment is another matter of concern; this topic is widely discussed in an excellent review by Kümmerer [12].

Given that some application strategies of antibiotics of agricultural use are the same employed for pesticides, the production of wastewaters with high loads of antibiotics becomes an issue that should be addressed. In particular, if such wastewaters are applied in a BPS, the antibiotics could exert inhibition in the degradation capacity of the system to remove pesticides.

This work aimed to assay the ability of a biomixture to remove several herbicides and to determine the effect of the antibiotic OTC on its performance. The effect of the OTC was evaluated on the respiration of the biomixture, the mineralization of chlorpyrifos and the simultaneous removal of three herbicides. Moreover, the ecotoxicity in the matrix during the removal of herbicides in the absence or co-application of OTC was also monitored.

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)) and linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea) were obtained from Chem Service (West Chester, Pennsylvania, USA). Commercial formulations of chlorpyrifos (Solver®48EC, 48% w/v), atrazine (Atranex® 90WG, 90% m/m), ametryn (Agromart® Ametrina 50SC, 50% w/v), linuron (Afalon® 45SC, 45% 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® 5WP, 5% w/w) were acquired from a local store. Radio-labeled chlorpyrifos (^{14}C-CLP; [ring-2,6-$^{14}C_2$]-chlorpyrifos; 4.38×10^9 Bq g^{-1}; radiochemical purity 98.99%; chemical purity 98.34%) was obtained from Izotop (Institute of Isotopes Co., Budapest, Hungary). Carbofuran-d$_3$ (surrogate standard, 99.5%) and linuron-d$_6$ (internal standard, 98.5%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Potassium hydroxide (analytical grade) and glucose were 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 Ruiz-Hidalgo et al. [13].

2.2. Biomixture

A biomixture containing coconut fiber, compost and soil pre-exposed to carbofuran at a volumetric composition of 45: 13: 42, respectively, was employed in the respiration, mineralization and removal assays. The composition of this biomixture was previously optimized in order to maximize the removal of carbofuran and to reduce the residual toxicity of the matrix [14].