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Phytotoxicity of pyrethroid pesticides and its metabolite towards *Cucumis sativus*

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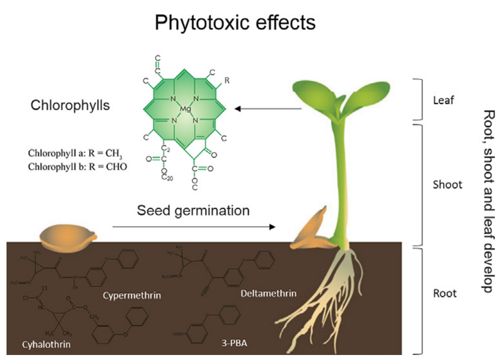
HIGHLIGHTS

- Potential phytotoxicity of pyrethroids and 3-PBA to soil.
- Pyrethroids and 3-PBA effect to *Cucumis sativus* seeds germination.
- Negative impact of cypermethrin and deltamethrin on seed development.
- Chlorophyll and carotenoids showed to be sensitive to some pyrethroids exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

Pyrethroid pesticides residues have been frequently detected in soils and have been recognized to contribute to soil toxicity. The phytotoxic impact of pesticides was evaluated in *Cucumis sativus* (*C. sativus*) seeds. Percentage of seed germination, root elongation, shoot length and leaf length were considered as endpoints to assess the possible acute phytotoxicity of soil by the exposure to pyrethroid pesticides (cypermethrin, deltamethrin and cyhalothrin) and its metabolite phenoxybenzoic acid (3-PBA), in a concentration range between 50 and 500 μg kg^{-1}. For germination percentage, it was only observed a negative impact when seeds were exposed to the metabolite. Cypermethrin showed impact in the three studied endpoints of seed development, while deltamethrin merely affected the root length. Concerning pigments content, it can be said that chlorophylls and total carotenoids median values increased for cypermethrin and deltamethrin. This increase was more pronounced to deltamethrin in joint effect with the organic solvent dimethyl sulphoxide (DMSO). When exposed to cyhalothrin and 3-PBA, no statistically significant differences were observed for *C. sativus* seeds to all the assessed endpoints of seed development and the investigated pigments content. This research brings new data concerning the relative sensitivity of *C. sativus* seeds to pyrethroids pesticides commonly found in agricultural facilities, as well as critical understanding and development of using *C. sativus* for phytotoxicity assessments efforts for pesticide exposures.

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1. Introduction

Pyrethroids pesticides are widely used as insecticides in agriculture, veterinary and domestic applications to control insect pests (Albaseer et al., 2011; Bronshtein et al., 2012). Synthetic pyrethroids were developed to preserve the insecticidal activity of pyrethrins and to enhance physical and chemical properties, as the stability to light (Gosselin et al., 1984). Pyrethroids differ from many other pesticides in that they have three typical characteristics: extreme hydrophobicity, rich stereochemistry (contain one to three chiral centers) and broad-spectrum high-level insecticidal activity. These pyrethroids represent a significant improvement when compared to other insecticide classes due to their very low non-target mammals and birds toxicity and better selectivity to target species (Luo and Zhang, 2011). The pyrethroids are the most common active ingredients in commercially available insect sprays and are the dominant pesticides for malaria control (Raghavendra et al., 2011; Ranson et al., 2011). Depending on the type of soil and the initial concentration the half-lives of pyrethroids in soil have been estimated to be between 17.1 and 52.1 and 8.3–105.3 days for cypermethrin and deltamethrin, respectively (Cycoń and Piotrowska-Seget, 2016).

Pyrethroids in the terrestrial environment occur mainly via spray drift but accidental spills and direct application to soil can also arise (Palmquist et al., 2012). Pyrethroids dynamic in soils is dependent on soil physical-chemical characteristics. Pyrethroids strongly bind to soil particles and organic matter due to their highly hydrophobic properties (Gu et al., 2008; Oudou and Hansen, 2002; Xu et al., 2015). These pesticides residues have been frequently detected in soils and sediments and have been recognized to contribute to sediment toxicity. Sediments in California's Central Valley were tested and in three-fourths of the toxic samples, pyrethroids exceeded concentrations expected to cause toxicity. Bifenthrin reached a maximum of 32 μg kg^{-1} in sediment much higher than the LC_{50} of 3–10 μg kg^{-1} for some invertebrates (*Hyalella azteca* or *Chironomus dilutus*). This study (Weston et al., 2013) reaffirms the contribution of pyrethroids to sediment toxicity even though sampling was not specifically focused on areas of high pyrethroids use. Pyrethroids were detected at maximum concentrations of 57.0 μg kg^{-1} before plow and 62.3 μg kg^{-1} during rice production in the soil in Mediterranean paddy fields, being resmethrin and cyfluthrin the compounds found at higher concentrations (Aznar et al., 2017). Pyrethroids presence was much higher in the sediments of creeks within a residential neighborhood near Roseville (Weston et al., 2005), where cyfluthrin, permethrin, bifenthrin, and cypermethrin were found at maximum concentrations of 169, 335, 437 and 736 μg kg^{-1}, respectively.

Pyrethroids in soil follow different pathways such as degradation, sorption-desorption, volatilization, uptake by plants and can also be transported into surface waters and groundwaters (Cycoń and Piotrowska-Seget, 2016). Microbial degradation of pyrethroids appears to be a significant breakdown route of such pesticides (Palmquist et al., 2012). The main process of environmental degradation of pyrethroids consists in the hydrolysis of carboxylester linkage that results most frequently in the production of cyclopropane acid and an alcohol moiety (3-phenoxybenzyl alcohol). The 3-phenoxybenzyl alcohol is rapidly converted to 3-phenoxybenzoic acid (3-PBA). 3-PBA frequently accumulates in the soil as well as the others metabolites referred above (Chen et al., 2011). Tyler et al. (2000) found that cyclopropane, permethrin acid, 3-phenoxybenzyl alcohol and 3-phenoxybenzoic acid, metabolites of environmental permethrin pyrethroid degradation, are of greater concern than their parent compound owing to their ability to interact with steroids hormone receptors. These metabolites in the environment can modulate and/or disrupt the endocrine systems of animals.

Pyrethroids raise environmental concerns due to their increasing and intensive use and potential effects on aquatic ecosystems as they are highly toxic to fish and invertebrates (Antwi and Reddy, 2015; Haya, 1989; Zhang et al., 2011). There are many studies documenting toxicological effects of pesticides on plants but studies tended to focus on herbicide effects in crop species (Gomes et al., 2017; Wagner and Nelson, 2014).

The increasing and widening use of pyrethroid insecticides cannot only cause residues in the soil but even lead to detrimental effects on plants and other non-target organisms, which necessitates a thorough understanding of their phytotoxicity. Research on the effects of pyrethroids on seed germination are scarce (Hanley and Whiting, 2005; Moore and Locke, 2012). Subsequently, a phytotoxic impact of these pesticides on soil should be assessed. Plant damage due to the application of pesticides is known as phytotoxicity. Pesticide phytotoxicity appears in several ways on plants, causing the studied compound an impact on plant characteristics. Plants are at their most sensitiveness to chemical's application during the early stages of life (Hewitt and Rennie, 1986). Inhibition of germination or on the root, shoot, and leaf development are the main areas of interest in studies on phytotoxicity (Kapanen and Itävaara, 2001). Seed germination and development can be affected by pyrethroid pesticides application. Hanley and Whiting (2005) reported that deltamethrin decreased the seedling growth of *Capsella bursa-pastoris* L. and *Poa annua* L. With increasing concentrations of cypermethrin and fenvalerate the germination rates of *Pennisetum pedicellatum* Trin showed a tendency to decrease (Dubey and Fulekar, 2011). Germination percentages of primary roots of *Glycine* max L. decreased with increasing cypermethrin concentration (Aksoy and Deveci, 2012). Visible phytotoxic effects can also occur, as chlorosis, necrosis, wilting and leaf and stem deformations (Wang and Williams, 1988). Cucumber and lettuce are the biological test species recommended by the U.S. Environmental Protection Agency for toxicity testing and environmental assessment (USEPA, 1996). The terrestrial plants assays for testing chemicals are considered valid when the following performance criteria are met for water controls: the seedling emergence must be at least 70%; the seedlings do not exhibit visible phytotoxic effects (e.g. chlorosis, necrosis, wilting, leaf and stem deformations); the plants exhibited only normal variation in growth and morphology for that species, and the mean survival of emerged control seedlings is at least 90% for the duration of the study (OECD, 2006).

The toxicity and the ecological risks in terrestrial environments of the mixtures of organic pollutants can be ascertained by the inhibition of photosynthesis efficiency (Gonzalez-Naranjo et al., 2015). Photosynthesis sustains nearly all life on Earth since it is largely responsible for providing oxygen present in Earth's atmosphere (Johnson and Portland Press, 2016). The measure of Chlorophyll-*a* (Ch *a*), Chlorophyll-*b* (Ch *b*) and total carotenoids (C x + c) are powerful tools to determine photosynthetic activity and so to evaluate the stress impact in plants (Zarco-Tejada et al., 2009). External factors can undesirable change and influence plants, causing different physiological responses (Ibanez et al., 2010). The Chlorophyll *a*/*b* ratio ($Ch_{a/b}$) is a conceivable indicator of nitrogen partitioning within a leaf since it can be positively correlated with the ratio of photosystem II cores to light harvesting chlorophyll-protein complex (Hikosaka and Terashima, 1995). Carotenoids and anthocyanins have also to be considered since they are the main pigments known to be involved in protecting plant organs from stress. Also, carotenoids additionally function as non-enzymatic antioxidants (Strzalka et al., 2003).

The aim of this study was to evaluate the phytotoxic effects of three synthetic pyrethroids (cypermethrin, deltamethrin, and cyhalothrin) and of one of their metabolites (3-PBA) in *Cucumis sativus* (cucumber) seeds. Given the sensitivity of seeds to chemicals, the effects of different concentrations (50, 125, 200, 350 and 500 μg kg^{-1} soil dry weight) of these compounds on seed germination, subsequent early growth of seedlings and pigments content of leafs were the main parameters followed. To the best of the authors' knowledge, this is the first study on the pyrethroid pesticides (cypermethrin, deltamethrin, and cyhalothrin) and its metabolite (3-PBA) phytotoxicity to *C. sativus* germination, the seedling grown and photosynthesis.