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Bioconcentration factor-based management of soil pesticide residues: Endosulfan uptake by carrot and potato plants

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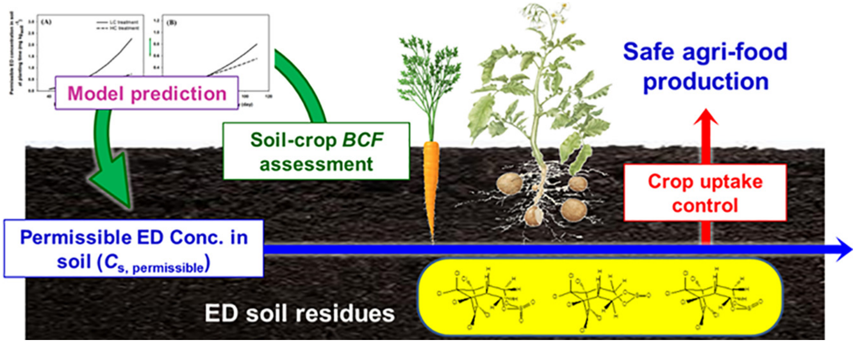
HIGHLIGHTS

- Endosulfan (ED) losses in crop-grown soils fit a double-exponential model.
- Crop ED uptake trends vary with plant compartment and starting soil ED levels.
- Bioconcentration factors (*BCFs*) decrease with time and fit first order kinetic models.
- *BCF* models could predict allowable soil ED residue levels for safe crop production.

GRAPHICAL ABSTRACT



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ABSTRACT

Uptake characteristics of endosulfan (ED), including α-, β-isomers and sulfate-metabolites, from the soils by carrot and potato plants were investigated to establish a method that may be used to calculate recommended permissible soil contaminant concentrations ($C_{s,\ permissible}$) at time of planting so that maximum residue level (MRL) standards are not exceeded. The residues of ED were analyzed in soils treated with ED at concentrations of either 2 or 10 mg kg soil^{-1} and in the plants (carrots and potatoes) grown in such soils for 60–90 d. Presence of plants increased ED dissipation rates in soils in patterns that were best fit to a double-exponential decay model (R^2 of 0.84–0.99). The ED uptake extent varied with type of crop, ED isomer, plant growth duration, and plant compartments. However, ED concentrations in all edible parts of crops eventually exceeded their maximum residue limits. Total ED bioconcentration factor (*BCF*), the ratio of soil ED concentration at planting time to that in edible part of each crop at harvest day, was found to decrease with time due to decreasing soil ED concentration and increasing plant biomass in a pattern that followed a first order kinetic model. Using this model, the $C_{s,\ permissible}$ values, specific to the soils used in this study, were calculated to be 0.32 and 0.19 mg kg soil^{-1} for carrots and potatoes, respectively. The results and methods developed in this study may be utilized as a prediction tool to ensure crop safety from pesticide residues.

1. Introduction

The pesticides used in the past to improve the quality and productivity of agricultural products often remain as residues in agricultural soils, a portion of which may be taken up by plant crops. This may pose a

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major concern with respect to the safety of these products for animal and human consumption. Many reports have shown that significant amounts of pesticide residues in agricultural soils can be taken up by plant roots, and transferred to edible parts, such as leaves and/or fruits (Esteve-Turrillas et al., 2005; Hwang et al., 2014, 2015a). In particular, because pesticide residues absorbed from soils are mostly retained in the roots of the plant, root and tuber crops may be the most susceptible to pesticide residue contamination (Paustenbach and Madl, 2008).

Over a million metric tons of carrots and potatoes, representative root and tuber crops, respectively, are produced globally each year (PotatoPro, 2017; World Carrot Museum, 2017). Soil residues of pesticides can be absorbed by plants either through their water uptake system (i.e. via roots) or via diffusion across their surface cuticle (Trapp et al., 2007; Juraske et al., 2011). In both potatoes and carrots, the dominant uptake route for soil pesticide residues is diffusion after cuticular penetration (Trapp et al., 2007). However, changes in the biomass of these crops during their cultivation period can make the residual concentrations of pesticides absorbed by the plants different. In addition, morphologic differences of the crops given that carrot is a root and potatoes are tubers may contribute to certain differences in their uptake mechanisms. Botanically, contrary to carrots, the potato tuber is a part of the stem and not connected to root systems and transpiration streams via the xylem vessel (Trapp et al., 2007). Although hydrophobic organic compounds can be loaded via the phloem vessel from the leaves, their translocations into the potato tubers via this pathway are negligible because there is no mechanism to retain the hydrophobic compounds in the phloem (Trapp et al., 2007; Juraske et al., 2011). These factors dictate the methods that are needed to predict concentrations of pesticide residues in different plants and at different times in their growth, so that an allowable harvest day can be determined, for each particular crop that will insure food safety.

Maximum residue level (MRL) standards of pesticides in food crops have been established to ensure the safety of crops (e.g. CODEX Alimentarius, 2017; European Commission, 2017; Ministry of Food and Drug Safety, 2017). In addition, based on the MRL standards, safe use guidelines for pesticides have been provided to crop producers (Korea Crop Protection Association, 2017; National Pesticide Information Center, 2017). However, methodological procedures to establish the guidelines generally do not consider impacts of soil pesticide residues on crop contaminant concentrations. If such soil pesticide residues are taken up by crops and combined with the pesticides applied in accordance with the safe use guideline, the combined pesticide residues in the crop could exceed the MRL. Thus, more detailed criteria are needed to inform crop producers how to manage crop planting and harvesting so as to meet the MRL standards.

Several countries, including U.S.A., Great Britain, and The Netherlands have tried to develop empirical model equations which predict residual pesticide crop uptake (e.g. U.S. Environmental Protection Agency, 1992; National Institute of Public Health and Environmental Protection, 2001; U.K. Environment Agency, 2008). These model equations are based on bioconcentration factors (*BCF*s), representing the ratio of the concentration of a pesticide in a crop to that in the soil in which it was grown. However, the developed model equations are often very complex and require considerable time and effort to obtain numerous empirical model parameters. In addition, experimental data needed to evaluate these model results are often lacking and the model equations are available only for a few soil—plant—pesticide systems. Thus, the overarching goals of this research are to better understand the controls on pesticide uptake by plants and to develop a simplified prediction models that may be used to guide pesticide management strategies based on *BCF* theory.

The organochlorine insecticide, endosulfan (6,7,8,9,10-hexachloro-1,5,5a,6,9,9,a-hexahydro-6,9-methano-2,3,4-benzodioxathiepin-3-oxide, ED), which resists degradation in soils due to the six chlorines in its structure, is a persistent organic pollutant (POP) that has been banned in most countries since the 5th Stockholm Convention in 2011. However, ED is still used in China, India, and several other countries due to the absence of alternative chemicals that can match its low cost and broad-spectrum efficacy for various insect pests including whiteflies, aphids, leafhoppers, Colorado potato beetles and cabbage worms (Stockholm Convention, 2009, 2017), and its residues are still detected in arable soils and agricultural products at significant levels (Park et al., 2013; Deepak et al., 2014; Ministry of Food and Drug Safety, 2016). Moreover, ED is present as both α- and β-isomers and as endosulfan sulfate (ED-sulfate), an oxidative metabolite of ED which is known to be even more toxic and persistent than its parent compounds (Goswami et al., 2009; Weber et al., 2010). For these reasons, ED is an excellent model pesticide compound to use in the study of long-term plant pesticide residue uptake patterns.

Here, uptake patterns of ED isomers and its metabolite from soils into carrot and potato compartments were assessed in relation to concentrations of ED in the soil and crop growth duration. In addition, using ED as a model compound, a model was developed to guide planting/pesticide management based on *BCF* theory.

2. Materials and methods

2.1. Chemicals

Analytical standards (>97% purity) of α-, β-isomers and sulfate metabolite of ED were purchased from Riedel-de Haën® (Deisenhofen, Germany) and dissolved in acetone. Commercial ED product used for the greenhouse experiment was 35% of the emulsifiable concentrate formulation containing α- and β-isomers in the ratio of 70:30 (w/w). Analytical grade organic solvents used were purchased from Burdick & Jackson Inc. (Muskegon, MI), and Florisil (F0127, 60–100 mesh) was acquired from Sigma-Aldrich Chemical Co. (St. Louis, MO).

2.2. Uptake experiment

Cultivars of carrot and potato used for uptake experiments were Shinheukjeon 5-chon and Jopung, respectively. All experiments were conducted in greenhouses located at Kimcheon, Republic of Korea with in-situ soils, and the distance between greenhouses for carrots and potatoes was approximately 1 km away. Soil samples collected from each greenhouse before uptake experiment were analyzed to verify that they contained none of ED residues. The pH, organic carbon content, and electric conductivity of the soil samples were analyzed using published methods (Rural Development Administration, 2000; Table S1). Treatment plots consisted of soils with no (control), low (2 mg kg soil^{-1}, LC), or high (10 mg kg soil^{-1}, HC) initial ED additions. Soil were planted with no crop, carrots or potatoes, and each of these 9 treatments were triplicated (i.e., $n = 3$).

The growth period for carrot was from August 10 to November 8, 2015, whereas for potato, growth was from January 9 to April 8, 2016. Each experimental plot was measured in area of 1 × 6 m. The LC and HC treatments were prepared by uniformly spraying 4 L aqueous ED solutions containing its commercial product of 3.4 and 17.1 g, respectively, on the soil surfaces of each experimental plot, and then by homogeneously blending the sprayed soil up to a soil depth of 10 cm. After 12 h following pesticide application, the soils were sampled to determine the initial ED concentrations, and then seeds of carrot and seed potatoes were added to the soil. The carrot seedlings were thinned to a plant to plant spacing of 10 cm. Seed potatoes were thinned to a 20 cm interval. During the crop growth period, no additional ED was applied, and water was supplied to the experimental plots at a flow rate of 2.0 L h^{-1} for 4 h every third day using a drip irrigation system. Temperature and humidity conditions in the greenhouse during the experimental period were maintained at 29.9 ± 3.8 °C and 64.8 ± 9.4%, respectively, for carrots, and 15.6 ± 2.9 °C and 64.3 ± 6.1%, respectively, for potato.