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Decreases in the bioconcentration of triclosan in wheat plants according to increasing amounts of biosolids added to soil

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ABSTRACT

The uptake of triclosan (TCS) and its metabolite methyl-triclosan (MTCS) by plants is poorly discussed in the current literature. The aim of this research was to analyze the extent of absorption of these compounds by the tissues of wheat plants by quantifying their bioconcentration factors (BCFs). Plants were grown for 30 days under controlled greenhouse conditions in two types of Chilean soil (Taqueral, TQ and Cuesta Vieja, CV) obtained from the metropolitan region of Santiago, Chile, that were amended with different amounts of biosolids containing indigenous and spiked TCS (10 mg kg^{-1}). Once the plants were harvested, both the root and the aerial parts of the plants were treated separately in each biomass sample. From the results, the extent of absorption of the compounds by the root was determined by measuring the BCF; the determined BCFs for the lowest and highest biosolid doses were 0.64 and 0.34 for TQ soil and 1.06 and 0.30 for CV soil, respectively. These decreases were significant (p *value* < 0.05). In the case of plants grown in soils treated with biosolids spiked with an extra amount of TCS, a higher amount of TCS was available (labile fraction) and higher BCF values were obtained. The contributions of organic matter from biosolid doses and pH of the matrix as well as the additional loads of TCS from the biosolids were evaluated through a multi-factorial design. A mathematical expression was derived using this model, which was applied to predict BCFs using data reported in the literature. Predicted values showed great variability mainly due to variations in the plant species and harvest times, indicating that these factors should also be included for the development of a more complete model.

1. Introduction

Various pharmaceutical and personal care products and their metabolites are continuously discharged into the environment through wastewater. Depending on their molecular structures and physicochemical properties, they can be degraded through the biological processes that occur at treatment plants or can be incorporated into the environment, causing toxic effects on living organisms. Triclosan (TCS) is one of these compounds, which due to its structural similarity to xenoestrogens, is classified as an endocrine disruptor (Cabana et al., 2007; Banihashemi and Droste, 2014; Provencher et al., 2014). Once methylated, TCS is transformed to methyl-triclosan (MTCS), which increases its lipophilicity and tends to bioaccumulate in lipid tissues; it is also less susceptible to photodegradation and is thus more stable in the presence of natural light (Chen et al., 2009).

TCS, which is released by personal care products, is one of the emerging contaminants that is present in higher concentrations in biosolids (Sabourin et al., 2012; Prosser et al., 2014; Sánchez-Brunete et al., 2010; Liu et al., 2009; Jachero et al., 2013). According to its K_{ow} value (4.8), TCS is a hydrophobic compound (Cha and Cupples, 2009), which tends to accumulate in the sediment or particulate matter of aqueous eco-systems (Aryal and Reinhold, 2011; Durán et al., 2012).

Biosolids are employed to amend agricultural soil, which benefits crops due to the contribution of nutrients, improvements in texture and other modifications of the physical properties of soil as well as through the incorporation of organic matter. In soils amended with biosolids, TCS has a half-life of 73–301 days (DT_{50}) and tends to degrade under aerobic conditions (Langdon et al., 2011). However, biosolids are also a source of trace amounts of organic and inorganic pollutants, which are discharged through domestic or industrial emissions; most of these pollutants are potentially toxic and generate problems linked to environmental pollution (Mikes et al., 2009) because the compounds present in the sludge can be mobilized to contaminate groundwater or be captured by living organisms. Consequently, this uptake affects the bioavailability of contaminants (Lavado et al., 2005). TCS accumulation in organisms has been reported in the literature including accumulation in plants (Zarate et al., 2012; Stevens et al., 2009; Macherius et al., 2012), humans (Allmyr et al., 2006) and animals (Coogan et al., 2007). In all these cases, the negative effects of TCS and its bioconcentration in each of the organisms were mentioned.

The plant uptake of organic compounds from the soil depends on their hydrophobicity, water solubility, vapor pressure, partition coefficient K_{ow}, concentration, persistence in the environment, environmental

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conditions and biological factors related to the ability of organisms to metabolize the organic compounds (Meylan et al., 1999; Staci et al., 1995). The presence of such compounds in some biological receptors tends to cause toxicity in the organism. This effect is generally related to the freely dissolved fraction (labile fraction) of the contaminant, which is available to be absorbed by biota and can be evaluated through measurements of bioconcentration factors (BCFs), (Wu et al., 2013; Wen et al., 2012; Mackay, 1982). BCFs are indicators that are widely used in risk analysis, toxicology studies and in protocols that test for chemicals that present potential hazards to the environment (Veith et al., 1979). Taking into account the fact that bioconcentration depends on the hydrophobicity of compounds (Wu et al., 2010), K_{ow} has been used as a fundamental parameter to estimate the bioconcentration of organic compounds that are introduced from the soil into root tissues (Paterson et al., 1994). Moreover, bioconcentration is pH-dependent and is affected by the pK_a of compounds (Wu et al., 2010). While most methods estimate BCFs based on physicochemical properties of the compounds, few are based on the studies of BCFs that consider matrix features. Thus, the aim of this study was to develop a model using a multilevel experimental design taking into account the influence of factors such as soil pH, dose of biosolid, and the presence of the analytes (TCS and MTCS); (either in indigenous form or added to the matrix). BCFs were evaluated for two emerging organic pollutants that were present in the biosolid samples, such as TCS and its metabolite MTCS. These results were compared with the uptake of the compounds by wheat plants that were evaluated through bioassays in soil with different doses of biosolids and in consideration of the two following scenarios: biosolids containing indigenous triclosan and biosolids spiked with an additional load of TCS.

2. Materials and methods

2.1. Reagents

Nano-pure water from a Barnstead water system (Dubuque, IA, USA) was used throughout this study. The TCS and MTCS (both 99.5% purity) analytes were purchased from Dr. Ehrenstorfer (Augsburg, Germany). A standard stock solution of the analytes was prepared in methanol (GC–MS/pesticides grade analysis; Fisher Scientific, Fair Lawn, NJ, USA). Irgasan® (containing a ≥97.0% TCS), purchased from Sigma–Aldrich (Milwaukee, WI, USA), was used to enrich the biosolid. Hexachlorobenzene (HCB, 99.5% purity), used as an internal standard, was purchased from Dr. Ehrenstorfer. $^{13}C_{12}$ Labeled triclosan, purchased from Wellington Laboratories (Ontario, Canada), was used as a surrogate standard. Nitrogen 5.0 and helium 5.0 were purchased from Linde (Santiago, Chile) and were used to evaporate the final extract and as the chromatographic carrier gas, respectively. Ethyl acetate, acetone, acetonitrile (HPLC-grade, 99.8% purity) and sodium chloride (99.5% purity) were purchased from Merck (Darmstadt, Germany). *N*-Methyl-*N*-(tert-butyldimethylsilyl) trifluoroacetamide (MTBSTFA) was purchased from Sigma–Aldrich (Milwaukee, WI, USA) and was used as a derivatizing agent.

2.2. Soil and biosolid characterization

Two soil samples were obtained from the metropolitan region in Chile: Taqueral (TQ) and Cuesta Vieja (CV) located at 6309.5 Km Lat. and 331.4 Km Long. UTM and 6292.9 km from Lat. and Long. 317.9 Km UTM, respectively.

The soil samples were collected at the surface level (0–10 cm). Compound samples from each sample site were air dried, passed through a 2 mm sieve and stored in plastic containers until use. The supernatants of soil-water suspensions with 1:2.5 (w/v) ratios were used to determine the pH of each sample. The organic carbon (OC) content of the soil and biosolid samples were determined with wet oxidation/digestion methods using dichromate, combined with a colorimetric method for the quantification of chromic oxide. Cation exchange capacities (CECs) were determined using a sodium acetate procedure at pH 7, and the sample textures were determined using the Boyoucus method (Zagal and Sadzawka, 2007).

The soil samples and biosolid properties were determined prior to the development of the bioassays; Table 1 shows the chemical features that were determined. The particle sizes showed that both soils were equivalent and had the same sandy-loam texture. The pH values of both soils were different; CV was slightly acidic and TQ was slightly alkaline. The soil samples showed differences in their organic matter content, with TQ having the highest content.

The biosolids resulting from anaerobic digestion were collected from a wastewater treatment plant in the Santiago Metropolitan Region. The biosolids were air-dried and passed through a 2-mm sieve. The biosolids were then mixed thoroughly into the soil samples at rates equivalent to 0, 30, 60, 90 and 200 Mg ha^{-1} and were incubated at 25 °C for 15 days under field capacity moisture conditions.

The biosolids were spiked with additional amounts of TCS dissolved in acetone (10 mg L^{-1}) using the following procedure: 500 g of the biosolid sample was placed in a separate 500 mL round flask, and an additional amount of TCS (10 mg kg^{-1}) was added using the commercial formulation, Irgasan®. The sample was evaporated in a rotary evaporator at 200 rpm for 24 h at room temperature in the dark to prevent photo-degradation of the compounds. The biosolids were then transferred to a dish and left to dry in the dark.

2.3. Greenhouse experiment

Wheat plants (*Triticum aestivum*) were grown in soil samples treated with natural biosolids and biosolids spiked with a commercial product-based TCS (Irgasan). Plastic pots were used for the plant assays. The pots were filled with the different soil samples and soil-biosolid samples with biosolids added to soils at 0, 30, 60, 90 and 200 Mg ha^{-1}. This study was performed in triplicate.

Each pot containing the equivalent of 500 g soil (dry weight) were irrigated to field capacity and allowed to stand for 15 days before sowing with wheat. A 10 g sample of wheat seed was planted in each pot. After the germination period (about one week), the automatic greenhouse lighting was set to produce a 14/10 h (day/night) cycle with a temperature of 25 ± 5 °C. The moisture content was controlled with daily watering with distilled water at 60–70% of the soil field capacity. After the growth period (30 days), the wheat plants were removed from the each pot and washed with distilled water. The roots and shoots of each pot were separated and oven-dried at 35 °C for 30 days.

2.4. Determination of TCS and MTCS in plant tissues

The roots and aerial parts of the plants were analyzed separately. Prior to analysis, each sample was weighed on a dry basis and the analytes were extracted using the matrix solid phase dispersion (MSPD) technique (Sánchez-Brunete et al., 2010). A 100 μL aliquot of a 2000 μg L^{-1} solution of $^{13}C_{12}$ TCS was added to each sample prior to the extraction as a method to control the quality of the recovery values.

The acetonitrile extract containing the concentrated analyte was then evaporated to dryness under a stream of N_2, and the residue was

Table 1
Characterization parameters of soil and biosoil samples.

Parameters	Taqueral	Cuesta Vieja	Biosolid
pH	8.2	6.5	6.9
OM (%)	5.9	3.3	–
Sand (%)	76	71	
Clay (%)	6	9	
Silt (%)	18	20	
OC (%)	3.4	1.9	28.1
Apparent density (g/cm^3)	1.25	1.12	
CEC (cmolkg^{-1})	22.3	18.5	71.6