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Inverse modeling of the biodegradation of emerging organic contaminants in the soil-plant system

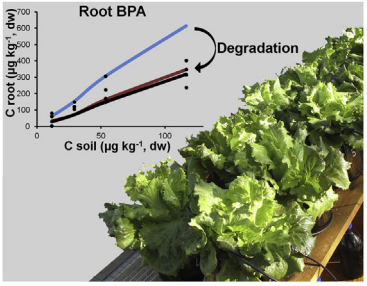
Carlos Hurtado [a], Stefan Trapp [b, *], Josep M. Bayona [a]

[a] Environmental Chemistry Department, IDAEA–CSIC, Jordi Girona 18-26, E-08034, Barcelona, Spain
[b] Technical University of Denmark, DK-2800, Kongens Lyngby, Bygningstorvet bd. 115, Denmark

HIGHLIGHTS

- Many emerging organic contaminants (EOCs) are polar and non-volatile, which makes plant uptake a likely process.
- EOCs differ widely in their degradation rates, leading to very different actual accumulation in plants.
- Biodegradation rates of EOCs were calculated for soil and fitted for roots and leaves.
- Bisphenol A and triclosan had the slowest degradation rate.
- Dissipation kinetics found via inverse modeling is not a conclusive proof for biodegradation and confirmation by experiments is needed.

GRAPHICAL ABSTRACT



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ABSTRACT

Understanding the processes involved in the uptake and accumulation of organic contaminants into plants is very important to assess the possible human risk associated with. Biodegradation of emerging contaminants in plants has been observed, but kinetical studies are rare. In this study, we analyse experimental data on the uptake of emerging organic contaminants into lettuce derived in a greenhouse experiment. Measured soil, root and leaf concentrations from four contaminants were selected within the applicability domain of a steady-state two-compartment standard plant uptake model: bisphenol A (BPA), carbamazepine (CBZ), triclosan (TCS) and caffeine (CAF). The model overestimated concentrations in most cases, when no degradation rates in plants were entered. Subsequently, biodegradation rates were fitted so that the measured concentrations were met.

Obtained degradation kinetics are in the order, BPA < CAF ≈ TCS < CBZ in roots, and BPA ≈ TCS < CBZ << CAF in leaves. Kinetics determined by inverse modeling are, despite the inherent uncertainty, indicative of the dissipation rates. The advantage of the procedure that is additional knowledge can be gained from existing experimental data. Dissipation kinetics found via inverse modeling is not a conclusive proof for biodegradation and confirmation by experimental studies is needed.

* Corresponding author. DTU Environment, Bygningstorvet bd. 115, DK-2800, Kgs. Lyngby, Denmark.
E-mail address: stt@env.dtu.dk (S. Trapp).

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1. Introduction

Pharmaceuticals, biocides and drugs as well as other chemicals from human use reach sewer systems and are partially removed during conventional wastewater treatment processes (Halling-Sørensen et al., 1998). By irrigation with reclaimed water, or sewage sludge amendment, these chemical residues may reach agricultural soils. Uptake into crops can lead to human exposure to such chemicals (Hospido et al., 2010). In the European Union, the environmental risk from pharmaceutical products is assessed only for veterinary drugs (EMA, 2011), and only few pharmaceuticals and drugs are regularly monitored according with the Watch List of the Water Framework Directive (Directive 2008/105/EC). Then, human exposure to emerging organic contaminants (EOCs) relies partly on scientific studies, and an increasing number of studies on their uptake into vegetables is reported (Wu et al., 2015; Miller et al., 2016).

Prosser and Sibley (2015) found no human health hazards from the plant uptake of the "majority of pharmaceuticals and personal care products". However, Malchi et al. (2015) stated that "current data are insufficient to support a comprehensive human health risk assessment" of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, or reclaimed water irrigation. Due to the high number of compounds potentially present in reclaimed water (Calderón-Preciado et al., 2011; Loos et al., 2013; Luo et al., 2014), prediction tools for pre-screening of chemicals and priority setting for safety assessments are of high value (Polesel et al., 2015). Prosser et al. (2014) examined the ability of two prediction models to estimate the uptake of pharmaceuticals and personal care products (PPCPs) into plants from sludge-amended soils. Predictions of plant uptake of PPCPs within one order of magnitude near the experimental results were achieved for some of the investigated compounds. Polesel et al. (2015) developed and tested a simulation tool for fate prediction from human pharmaceuticals down the drain through a sewage treatment plant and via sludge amendment and irrigation to agricultural fields and crops. However, simulations were performed disregarding degradation in plants. To reduce discrepancies between model predictions and measurements, the authors stressed the need for more measured input parameters (e.g., K_d) and kinetics of biotransformation in plant tissues.

For polar compounds, efficient translocation in xylem of plants can be expected (Trapp, 2007; Dettenmaier et al., 2009), leading to accumulation in leaves, if no losses occur. Biodegradation has been identified as among the most relevant dissipation processes of chemicals from plants (Fantke et al., 2012; Jacobsen et al., 2015), but is often unknown or uncertain and depends on a number of factors, such as species and temperature (Fantke and Juraske, 2013; Fantke et al., 2014; Jacobsen et al., 2015). Methods to measure metabolism in soil and plants have been developed early, typically employing the use of ^{14}C-labeled compounds to close the mass balance (Trapp et al., 1990; Kästner et al., 2014). There are also OECD guidelines for pesticide metabolism in crops to elucidate the degradation pathway available (i.e. OECD Tests Nr. 501, 502). The drawback is that studies with hot labels are expensive, and safety issues arise. These safety issues can be solved by using stable isotopes (^{13}C and ^{15}N), but require IRM-MS equipment, if isotopically labeled compounds are available at all.

An alternative method to assess biodegradation that has rarely been attempted is the use of inverse modeling. Hereby, predictable loss due to physical-chemical processes (volatilization, translocation, dilution) is contrasted with measured dissipation. The difference is contributed to biodegradation. This method cannot prove degradation but can help to quantify loss processes (Jacobsen et al., 2015).

The kinetics of biodegradation affects the relation between concentrations in plants and soil. First-order degradation kinetics, either in soil or in plants, will change the slope of the trend line (lower for degradation in plants, higher for degradation in soil), but the relation will remain linear. In a study with lettuce grown under controlled conditions and irrigated with water containing eight emerging organic contaminants (EOCs), Hurtado et al. (2016) obtained mostly linear correlations between watering concentrations and concentrations measured in roots and leaves. Besides hydrophobicity (log D_{OW}) of chemicals, their persistence was identified as a key determinant for plant uptake and accumulation of the EOCs.

In this study, we supplemented a standard plant uptake model (Rein et al., 2011) with different degradation kinetics for soil and plant. The model was parameterized to simulate the uptake experiments of emerging organic contaminants into lettuce performed by Hurtado et al. (2016). Degradation rate constants in soil were derived from the measured concentrations, while rates in leaves and roots were fitted, based on the difference between the model prediction (without degradation) and the measured data. The resulting rates were compared to data from literature.

2. Materials and methods

2.1. Experimental section

Experiments were conducted in a glass greenhouse located in Viladecans (Barcelona, Spain) as described in Hurtado et al. (2016). Briefly, lettuce (*Lactuca sativa*) was planted in pots in a mixture of perlite and sand (2:1 v/v, approx. 1.2 kg) and watered with Hoagland nutrient solution (Hoagland and Arnon, 1950) diluted 1:1 with rain water. A dose of 50 mL of irrigation water was applied to each experimental unit per day. The number of daily irrigations was regulated to keep water in the soil below field capacity, thereby preventing leachate production.

After 40 days, EOCs were added to soil. Five treatments consisted of direct application of 0, 14, 35, 70 and 140 μg of eight EOCs per experimental unit in eight applications during 28 days. Taking into account the soil substrate mass in each experimental unit, this corresponds to an average nominal initial concentration in the substrate of 0, 11.7, 29.2, 58.3 and 116.7 μg kg^{-1} dw. After 28 days, substrate, roots and leaves of lettuces were separated and analyzed. The data used in this study can be found in the SI and are also reported in Hurtado et al. (2016).

The EOCs measured in the experimental study were bisphenol A, caffeine, carbamazepine, ibuprofen, propranolol, sulfamethazine, triclosan and tonalide. All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA), except tonalide from Ventós (Sant Just Desvern, Spain). The extraction of EOCs from vegetal tissue and substrate and the analytical parameters are listed in Hurtado et al. (2016). The properties of the compounds are listed in Table 1.

2.2. Model section

The plant uptake model is based on the commonly used "standard model" for plant uptake (Legind and Trapp, 2009; Legind et al., 2011; Rein et al., 2011; Trapp, 2015). Modifications were introduced to consider different degradation kinetics. This version of the model is primarily designed for neutral compounds. As long as the fraction of ionic molecules is small, ionization only slightly affects the outcome when measured K_d-values are used. PROP, IBU and SMT were not included in the plant uptake simulations because the ionization prohibits the use of this model version. TON was excluded because of its high volatility. In a separate approach, *Michaelis-Menten* degradation kinetics in roots and leaves was calculated, but for mathematical reasons with initial (constant)