Elsevier Editorial System(tm) for Journal of Hazardous Materials
Manuscript Draft

Manuscript Number:

Title: Estimate of uptake and translocation of emerging organic contaminants from irrigation water concentration in lettuce grown under controlled conditions

Article Type: Research Paper

Keywords: plant uptake; emerging contaminants; rhizosphere; bioconcentrantion factors; degradation; translocation factor

Corresponding Author: Dr. Josep Maria Bayona,

Corresponding Author's Institution:

First Author: Carles Hurtado

Order of Authors: Carles Hurtado; Carmen Domínguez; Lorea Pérez-Babace; Núria Cañameras; Jordi Comas; Josep Maria Bayona

Abstract: The widespread distribution of emerging organic contaminants (EOCs) in the water cycle can lead to their incorporation in irrigated crops, posing a potential risk for human consumption. To gain further insight into the processes controlling the uptake of organic microcontaminants, Batavia lettuce (Lactuca sativa) grown under controlled conditions was watered with EOCs (e.g., non-steroidal anti-inflammatories, sulfonamides, β−blockers, phenolic estrogens, anticonvulsants, stimulants, polycyclic musks, biocides) at different concentrations (0 - 40 μg L-1). Linear correlations were obtained between the EOC concentrations in the roots and leaves and the watering concentrations for most of the contaminants investigated. However, large differences were found in the root concentration factors (= 0.27 - 733) and leaf translocation concentration factors (= 0 - 3) depending on the persistence of the target contaminants in the rhizosphere and the specific physicochemical properties of each one. Of these properties, DOW, KOA and KAH were the best descriptors for predicting potential EOC uptake by lettuce grown in a low-interaction soil (sand:perlite) and leachate-less culture. With the obtained dataset, a simple predictive model based on a linear regression and the root bioconcentration and translocation factors can be used to estimate the concentration of the target EOCs in leaves based on the dose supplied in the irrigation water or the soil concentration. Finally, enantiomeric fractionation of racemic ibuprofen from the initial spiking mixture suggests that biodegradation mainly occurs in the rhizosphere.

COVER LETTER

Dear editor,

The manuscript entitled *Estimate of uptake and translocation of emerging organic contaminants from irrigation water concentration in lettuce grown under controlled conditions* has not been previously published, in whole or in part, and that it is not under consideration to any other journal. All authors are aware of the manuscript submission, and accept responsibility for, this manuscript.

Although the uptake of organic contaminants in crops has already been reported, the processes involved in the rizosphere and the uptake processes are largely unknown. The originality of this manuscript is to assess the relationship between the concentration in the irrigation water and plant uptake for a broad spectrum of organic contaminants with a wide range of physical-chemical properties including both neutral and ionized. Soil, root and leaves were independently analyzed and bioconcentration and translocation factors. For the first time, volatilization from soil and foliar sorption as a route of contaminant uptake from irrigation water is proposed for polycyclic musk fragrances occurring in irrigation water. Furthermore, the enantiomeric fraction of ibuprofen in soil, roots and leaves gives some insights in the relative contribution of biotic degradation processes in the different plant compartments (roots & leaves). The environmental relevance of this study is related to the fate of PPCPs in the soil-plant environment where multiple processes occur and to study their significance demands a systematic study under well-controlled conditions that could be replicate elsewhere.

Hoping to hear from you soon.

Yours sincerely,

Dr. **J.M. Bayona**,
Research Professor

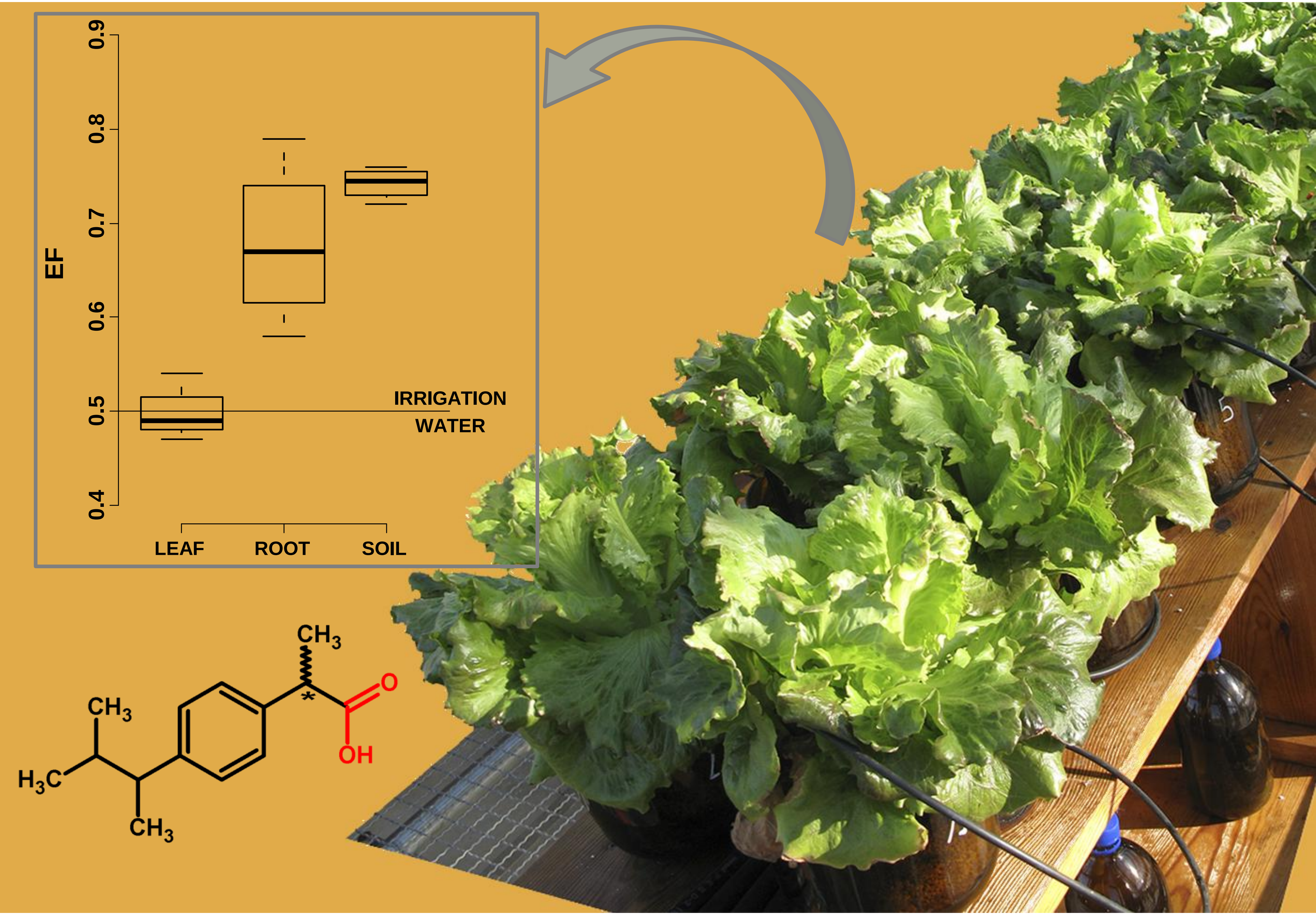
Coauthors:
MSc Carlos Hurtado. IDEA-CSIC
Dr. Carmen Domínguez. IDEA-CSIC.
Ms. Lorea Perez. IDAEA-CSIC.
Dr. Núria Cañameras. DEAB-UPC.
Dr. Jordi Comas. DEAB-UPC.

NOVELTY STATEMENT

For the first time, linear correlations were obtained between the EOC concentrations in the roots and leaves and the watering concentrations for most of the contaminants investigated under controlled conditions in a low interaction soil.

The enantiomeric fraction (EF) of ibuprofen shows significant changes depending on the compartment suggesting that different biodegradation pathways.

Graphical Abstract



Highlights (for review)

- Linear uptake of EOCs in lettuce was observed along their irrigation concentration.
- EOCs translocation factor is dependent of their Dow.
- Volatilization and foliar uptake is significant pathway for fragrances.
- IBU biodegradation in root and leaves was confirmed by its changes in EF.

Estimate of uptake and translocation of emerging organic contaminants from irrigation water concentration in lettuce grown under controlled conditions

Carlos Hurtado[a], *Carmen Domínguez*[a], *Lorea Pérez-Babace*[a], *Núria Cañameras*[b], *Jordi Comas*[b], *Josep M. Bayona**, [a]

[a]*Environmental Chemistry Department, IDAEA–CSIC, Jordi Girona 18-26, E-08034 Barcelona, Spain*

[b]*Department of Agri-Food Engineering and Biotechnology DEAB-UPC, Esteve Terrades 8, Building 4, E-08860, Castelldefels, Spain*

KEYWORDS: plant uptake, emerging contaminants, rhizosphere, bioconcentrantion factors, degradation, translocation factor.

ABSTRACT

The widespread distribution of emerging organic contaminants (EOCs) in the water cycle can lead to their incorporation in irrigated crops, posing a potential risk for human consumption. To gain further insight into the processes controlling the uptake of organic microcontaminants, Batavia lettuce (*Lactuca sativa*) grown under controlled conditions was watered with EOCs (e.g., non-steroidal anti-inflammatories, sulfonamides, β–blockers, phenolic estrogens, anticonvulsants, stimulants, polycyclic musks, biocides) at different concentrations (0 - 40 μg L^{-1}). Linear correlations were obtained between the EOC concentrations in the roots and leaves and the watering concentrations for most of the contaminants investigated. However, large differences were found in the root concentration factors (R_{CF_i} = 0.27 - 733) and leaf translocation concentration factors (L_{TCF_i} = 0 – 3) depending on the persistence of the target contaminants in the rhizosphere and the specific physicochemical properties of each one. Of these properties, D_{OW}, K_{OA} and K_{AH} were the best descriptors for predicting potential EOC uptake by lettuce grown in a low-interaction soil (sand:perlite) and leachate-less culture. With the obtained dataset, a simple predictive model based on a linear regression and the root bioconcentration and translocation factors can be used to estimate the concentration of the target EOCs in leaves based on the dose supplied in the irrigation water or the soil concentration. Finally, enantiomeric fractionation of racemic ibuprofen from the initial spiking mixture suggests that biodegradation mainly occurs in the rhizosphere.

1. Introduction

In a context of climate change and a burgeoning world population,[1] the pressure on water resources will grow, particularly in arid and semiarid regions. Agriculture is the sector that consumes the most water at the global level, accounting for approximately 70% of total consumption.[2]

However, emerging organic contaminants (EOCs) such as pharmaceuticals and personal care products (PPCPs) have been detected in surface water used for irrigation in agriculture.[3, 4] It is thus necessary to assess the behavior, fate, and health risks these compounds pose.

Depending on their physicochemical properties, EOCs transferred to soil through irrigation can be volatilized, sorbed to soil, mobilized to groundwater, biodegraded in the rhizosphere, and taken up by crops.[5] Some studies have already shown the potential uptake of pesticides, veterinary medicines, and other EOCs by crops in different experimental setups. For example, in *in vitro* experiments,[6, 7] plants like cabbage and lettuce have been shown to take up certain anticonvulsants (e.g., carbamazepine), antibiotics (e.g., trimethoprim), and non-steroidal anti-inflammatories (e.g., ibuprofen and naproxen) from the nutrient solution. Other studies conducted in greenhouse conditions have demonstrated that crops watered with treated wastewater (TWW) or soil amended with biosolids can uptake pollutants such as non-steroidal anti-inflammatories (e.g., ibuprofen, naproxen, flunixin), fragrances (e.g., galaxolide, ambrettolide), herbicides and pesticides (e.g., simazine, DDT), and PPCPs (e.g., triclosan, triclocarban, carbamazepine).[8-11] Field trials have demonstrated that vegetables (celery, carrot, lettuce, cabbage, and cucumber) were able to take up PPCPs (e.g., primidone, carbamazepine, dilantin)[12] and fragrances (e.g., galaxolide,[11] methyl dihydrojasmonate) from TWW spiked with PPCPs and that alfalfa and apple trees could take up anticonvulsants (e.g., carbamazepine) from reclaimed water.[13]

As PPCPs include a wide spectrum of compounds exhibiting different physicochemical properties, distinct behaviors should be expected. Accordingly, highly hydrophobic compounds such as polycyclic musks are strongly sorbed to the soil organic matter and thus become less bioaccessible to crops, while more hydrophilic persistent compounds, such as carbamazepine, exhibit a high uptake potential for many crops.[14, 15]

Several empirical and process-based models have been developed to try to predict the concentration of metals[16-18] and organic compounds in plants, including polycyclic aromatic hydrocarbons (PAHs),[19] organophosphates,[20] and certain PPCPs (e.g., carbamazepine, cimetidine, triclocarban),[21] among others. However, while useful for building a theoretical framework for risk assessment, some of these models,[22, 23] such as the dynamic plant uptake model,[22] are too data intensive to assess the uptake of emerging contaminants in practice.[24] Therefore, more experimental studies are needed to identify the most relevant processes.

For neutral compounds, lipophilicity is the most widely used molecular descriptor. In 1982, Briggs et al.[25] showed that non-polar compounds followed a Gaussian-like distribution between the transpiration stream concentration factor (TSCF) and log K_{OW}, with a maximum value between 1 and 3. However, this behavior is not found with ionic or ionizable compounds.[26] In fact, based on the pH of the soil and the pH of the plant xylem, ionizable compounds or weak electrolytes can occur in anionic, cationic, and zwitterionic forms. Consequently, these ionic compounds can be taken up as counter ions or by the ion trap effect, which occurs when a compound is neutral and can be dissociated inside the plant cells.[27, 28]

Several studies have reported the use of rhizobacteria to promote plant growth and in phytoremediation.[29] Among them, endophytic bacteria[30, 31] were recently proposed for the biodegradation of organic pollutants.[32-35] Moreover, it is well established that biotic processes are enantioselective, affecting one of the enantiomers of chiral contaminants (e.g., ibuprofen).[36] Therefore, the enantiomeric fractionation of chiral contaminants can be used to assess the occurrence of biotic processes in environmental compartments.

This study aimed to evaluate the uptake of eight EOCs with a broad range of physicochemical properties supplied at four concentrations to lettuce (*Lactuca sativa*) through soil with a low colloidal fraction. The EOCs were selected based on their high detection and occurrence in all types of waters and their effects in humans. For example, compounds with an endocrine disruptor activity such as bisphenol A (BPA),[37-40] persistent and highly bioaccumulable compounds such as carbamazepine (CBZ),[41-43] propranolol (PROP)[44-46] and tonalide (TON).[47-51] Moreover, compounds which main concern is the bacterial resistance like the veterinary antibiotic sulfamethazine (SMT)[52-56] and the biocide triclosan (TCS) present in many care products.[57-60] Finally, the biological active compound caffeine (CAF) which is also recognized as a contaminant of freshwater and urban aquatic environment[61-65] and ibuprofen (IBU) which is one of the most used analgesics and it has been detected also in most of the aquatic system.[66-68]

The concentration of the supplied EOCs in the soil close to the roots, in the roots themselves and in the leaves was determined in order to study the processes of incorporation and translocation of the different EOCs. Finally, a simplified model was developed using the data for all four concentrations to predict the concentration of a given EOC in the leaves for a specific initial treatment, which could be useful for risk assessment. Moreover, the lettuce was watered below the soil field capacity so as not to generate leachates.

2. Materials and methods

2.1 Experimental Layout

The experiment was carried out in a glass greenhouse located at the Agròpolis-UPC agriculture experimental station (41º 17' 18" N, 2º 02' 43" E) in Viladecans (Barcelona, Spain). The experimental units consisted of 2.5 L cylindrical amber glass pots (Ø = 15 cm and 20 cm high) fitted with a tubing outlet at the bottom (Ø = 3 cm). In order to minimize potential interactions between EOCs and soil colloids, the experimental units were filled with 2 L of a mixture of perlite and sand (2:1, v/v, average dry weight 1.2 kg). One Batavia lettuce (*Lactuca sativa*, cv. Arena) seedling was planted in each experimental unit and watered with the Hoagland and Arnon[69] solution prepared with harvested rainwater (pH = 5.5). A nutrient solution was supplied through an on-line drip irrigation system. 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 at field capacity, thereby preventing leachate production.

Treatments consisted of the direct application of 14, 35, 70 and 140 µg of eight EOCs per experimental unit. This procedure made it possible to avoid possible adsorption of the applied products by the irrigation tubing and associated biofilm. Taking into account the irrigation water supplied, this corresponds to an average EOC concentration in the irrigation water (IW_C) of 4, 10, 20 and 40 µg L^{-1}, and taking into account the soil mass in each experimental unit, it corresponds to an average concentration in the soil (S_C) of 11.7, 29.2, 58.3 and 116.7 µg kg^{-1}. The control consisted of planted experimental units to which no EOCs were applied.

Treatments were distributed among eight applications over the course of four weeks, starting six weeks after planting. The experiment had a total duration of 10 weeks. The treatments and control were replicated four times. The selected EOCs were as follows: bisphenol A (BPA, 99%), caffeine (CAF, 99%), carbamazepine (CBZ, 99%), ibuprofen (IBU, 98%), propranolol (PROP, 99%), sulfamethazine (SMT, 99%), triclosan (TCS, 97%), and tonalide (TON, 97 %). The BPA, CAF, CBZ, IBU, PROP, SMT, and TCS were purchased from Sigma-Aldrich (St. Louis, MO, USA), and the TON from Ventós (Sant Just Desvern, Spain). Table 1 shows their structure and physicochemical properties.

2.2 Analysis of Vegetable Tissues and Substrate

Upon conclusion of the experiment (at 10 weeks), the plants were harvested and the substrate close to roots, the roots themselves, and the entire aerial part of the plant (mostly leaves) were analyzed.

After the sampling was performed, the roots were watered with deionized water to remove the adhered perlite-sand mixture. The roots and leaves were comminuted with liquid nitrogen and stored at -20ºC until analysis. The extraction of vegetable tissue was performed as reported elsewhere.[70] Briefly, a matrix solid-phase dispersion method was applied to the vegetable tissue. A 0.5 g aliquot of plant tissue (root or leaf) was spiked at 10 ng g^{-1} with a mixture of surrogates (10 11-dihydrocarbamazepine, DHCBZ; 2,2′-dinitrobiphenyl, DNBP; fenoprop, FEN; sulfamethoxazole SMX, and tonalide-d3,TON-D3 (SI, Section 1.1)). The sample was then blended with florisil, Na_2SO_4, Na_3-citrate dihydrate, NaCl, Na_2H-citrate sesquihydrate, and Hydromatrix using a pestle. The mixture was extracted with a mixture of acetone:hexane (1:1, v/v) using a pressurized solvent extraction (PSE) apparatus (Applied Separations (Allentown, PA, USA)). Samples were extracted with two 14-minute cycles at 104 ºC and 110 bar. Neutral-basic and acid fractions were obtained by solvent partitioning at neutral and acid pH respectively. The final extracts were analyzed by GC and LC coupled to tandem mass spectrometry.

Extraction of the EOCs in the soil close to the roots was performed as follows: a 1 g aliquot spiked with the same mixture of surrogates was mixed with 0.5 g of sodium sulfate anhydrous, equilibrated for 1 h, and extracted twice with 10 mL of an acetone:hexane (3:1, v/v) mixture for 15 min by sonication. A third extraction with 10 mL of methanol was performed. The resulting extracts were combined, evaporated to 2 mL, and dried by percolation through an anhydrous sodium sulfate column. The extraction solvent mixture was replaced with ethyl acetate prior to the samples' injection in the GC system.

The aliquots of the sample extracts were analyzed first using an EI GC-MS/MS Bruker 450-GC gas chromatograph coupled to a Bruker 320-MS triple-stage quadrupole mass spectrometer (Bruker Daltonics Inc., Billerica, MA, USA). Qualitative and quantitative analyses were performed based on retention time and the selected reaction monitoring (SRM) mode of two product ions, as well as the ratio between the product ions (Table S1).

Another sample extract aliquot was evaporated and reconstituted with methanol:water (20:80, v/v). SMT and PROP were analyzed by LC-MS/MS using a TSQ Quantum triple-stage quadrupole mass spectrometer equipped with an ESI source (Thermo Fischer Scientific, San Jose, CA, USA). Qualitative and quantitative analysis was performed based on retention time and the selected reaction monitoring (SRM) mode of two product ions, and the ratio between the product ions was determined by confirmation (Table S2). The limits of detection and quantification for all the targeted analytes and matrices are given in Table S3, and the recoveries are given in Table S4.

Finally, sample extract aliquots were subjected to chiral derivatization of IBU as described by Hashim and Khan.[71] The full procedure is described in the SI (Section 1.4).

2.3 Data Analysis

Standardized Concentrations

The standardized concentrations of the tested EOCs in the soil close to the roots (SR_{SC}) were calculated as follows:

$$SR_{SC} = \frac{1}{4} \times \sum_{T_i}^{4} \frac{SR_{C_i}}{S_{C_i}} \quad \text{[Eq. 1]}$$

where T_i stands for the treatment applied (1 to 4), SR_C is the concentration of a given EOC in the soil close to the roots, and S_C is the initial soil concentration (11.7, 29.2, 58.3 or 117 μg kg^{-1}). The standardized concentrations in the roots (R_{SC}) and leaves (L_{SC}) were calculated similarly.

Enantiomeric Fraction (EF)

Many EOCs are produced synthetically as racemic mixtures. Hence, 50% of the compound is the *R* form, and 50% the *S* form. The enantiomeric fraction is a descriptor of enantiomeric (chiral) mixtures.[72] Although in the natural environment, many physical processes are not enantioselective (e.g., hydrolysis, photolysis), microbial degradation and biological metabolism can be.[36, 73] The EF was calculated as described in Equation 2.

$$EF = \frac{S}{S+R} \quad \text{[Eq. 2]}$$

Bioconcentration and Translocation Factors

The concentration factor for soil close to the roots in treatment *i* (SR_{CF_i}) was calculated as follows:

$$SR_{CF_i} = \frac{SR_{C_i}}{S_{C_i}} \quad \text{[Eq. 3]}$$

where SR_{C_i} and S_{C_i} are the concentration of a given EOC in the soil close to the roots and the average concentration of EOC for the soil mass in treatment *i*, respectively.

Likewise, the root concentration factor in treatment *i* (RCF_i) was calculated as follows:

$$R_{CF_i} = \frac{R_{C_i}}{S_{C_i}} \quad \text{[Eq. 4]}$$

where R_{C_i} is the concentration in the roots in treatment *i*.

For each EOC, the linear regression coefficient (assuming an intercept of zero) of R_{C_i} over S_{C_i} was also calculated (b_{R_C/S_C}).

Finally, the leaf translocation concentration factor (L_{TCF_i}) was calculated as follows:

$$L_{TCF_i} = \frac{L_{C_i}}{R_{C_i}} \quad \text{[Eq. 5]}$$

where L_{C_i} is the concentration in the leaves in treatment *i*.

Modeling of Concentration in Leaves

The predicted concentration of a given EOC in the leaves (L'_{C_i}) was calculated by means of the following equation:

$$L'_{C_i} = L_{TCF_m} \times b_{R_C/S_C} \times S_{C_i} \quad \text{[Eq. 6]}$$

where L_{TCF_m} is the average leaf translocation factor, and b_{R_C/S_C} is the linear regression coefficient of R_{C_i} over S_{C_i} over the course of the different treatments *i*.

L'_{C_i} could also be expressed relative to the average concentration of a particular EOC in the irrigation water (IW_{C_i}) in a given treatment *i* as follows:

$$L'_{C_i} = L_{TCF_m} \times b_{R_C/IW_C} \times IW_{C_i} \quad \text{[Eq. 7]}$$

where, b_{R_C/IW_C} is the linear regression coefficient of R_{C_i} over IW_{C_i} over the course of the different treatments *i*. This model has been validated for soil with very low CEC and no leachates.

2.4 Statistical Analysis

The regressions, analysis of variance (ANOVA), and subsequent mean separation (LSD) were conducted in R (R Development Core Team, 2015).[74]

3. RESULTS

3.1 Occurrence of EOCs in the Different Compartments

3.1.1 Concentration in the Soil Close to the Roots

The concentrations of the tested EOCs in the soil close to the roots (SR_C) were lower than in the roots themselves (R_C) or in the leaves (L_C). They ranged from 0.3 to 167 ng g^{-1} dw depending on the product and dose applied (Table 1). Overall, TCS was the EOC to exhibit the highest concentration, while SMT had the lowest; their standardized concentrations (Eq. 1) were 1.47 ± 0.45 and 0.03 ±0.01, respectively (Figure 1A).

3.1.2 Concentrations in the Roots

Generally, the average concentration in the roots (R_C) was between 2.6 and 150 times higher than in the soil close to the roots (SR_C). In absolute terms, R_C varied widely, from below the LOQ to 1630 ng g^{-1} dw, again depending on the EOC and treatment (Table 1). Overall, CBZ had the highest concentrations, and IBU, the lowest; their standardized concentrations were 9.67 ± 1.99 and 0.90 ± 0.78, respectively (Figure 1B).

3.1.3 Concentration in the Leaves

Overall, EOC concentration in the leaves (L_C) averaged between 0.5 and 110 times lower than in the roots. The concentration varied, depending on the EOC tested and the treatment used; however, the concentration of CBZ in the leaves was much higher than that of the other products (Figure 1C).

3.2 Enantiomeric Fractionation of IBU

IBU is sold as a racemic mixture; however, in the soil close to the roots, the *S* enantiomer predominated over the *R* enantiomer (EF = 0.74 ± 0.02), which means that the *R* form was degraded more easily than the *S* form. In the roots, the *S* enantiomer was still predominant, although less so than in the S_R, as the EF decreased (0.68 ± 0.09). Finally, in the leaves, a complete racemization (EF = 0.50 ± 0.03) was observed (Figure 2).

3.3 Bioconcentration Processes

TCS was the only tested EOC to have a concentration factor in the soil near the roots (SR_{CF}) greater than 1; its average was 3.5. The SR_{CF} of the remaining EOCs was significantly lower, averaging between 0.1 and 0.4 (Figure 3A).

The root concentration factor (R_{CF}) values were much greater than the SR_{CF}. Their values ranged from 0.43 to 11.7. The EOC with the highest R_{CF} was CBZ (average of 9.3), followed by PROP (average of 6.0) (Fig 3B). The other EOCs tested exhibited much lower values. For IBU, the R_{CF} clearly increased as larger and larger doses were applied; the opposite was true of PROP. For TON, at the lower application rate, the value of R_{CF} was very low. It then stabilized at a greater value as the application rates increased. For the remaining products, the values of R_{CF} were relatively independent of the application rates (Figure 3B).

It is noteworthy that the leaf translocation concentration factor (L_{TCF}) for CBZ is much higher (average of 3.4) than that of the remaining products, which, on average, are lower than 1.

The L_{TCF} values are also slightly dependent on the concentration, declining at the highest concentrations (Figure 3C).

3.3 *Modeling the uptake of EOC*

The concentration of the tested EOCs in the roots showed a strong linear relationship with the application rate expressed as the average concentration in the soil (S_C) or in the irrigation water (IW_C) (Figure 4). The coefficients of determination (R^2) always take values higher than 90%. This strong linear relationship is held even for IBU, PROP, and TON, for which the R_{CF} clearly depends on the rate of application. The high values of the slopes indicate the ease with which most products are taken up by the roots. Moreover, translocation from roots to leaves remained relatively stable regardless of the treatments applied, as shown by the values of the translocation concentration factors (Fig. 3C).

The above considerations make it possible to build a simplified model to predict the concentration of a given EOC in the leaves (L'_C) for a specific treatment *i*, multiplying the average leaf translocation concentration factor (L_{TCF_m}), the slope of the linear relationship of the root concentration (b_{R_C/S_C}) over the mean soil concentration of the given EOC, and the mean concentration of the EOC in the soil in a given treatment *i* (S_{C_i}) (Eq. 6)

Figure 5 shows that there is strong agreement between the predicted concentration values in the leaves using Equation 6 and the observed values (R^2 = 0.9985). Depicted values are located very close to the bisecting line, even for EOCs like BPA, IBU, and TCS, for which the linear relationship between the concentration in leaves and the initial applied concentration is less strong (Figure 4).

4. Discussion

Although the uptake of pharmaceuticals by plants from irrigation water and biosolids has been widely documented,[3, 9, 12, 13, 15, 75-80] the exact soil-root-plant system processes involved in this uptake are not yet well understood. This paper looked at the uptake of several EOCs by lettuce when the plants are grown in a soil with a very low cation exchange capacity (CEC) and the dose of irrigation is adjusted to prevent leaching. Therefore, the permanence of an EOC in the soil should depend on its recalcitrance and the ease with which it is taken up by roots. Volatilization from the soil can also be a significant transport pathway for semivolatile EOCs such as TON (log K_{AW} = -2.04, log K_{OA}= 7.95, Table 1). According to the non-steady state model for both hydrophilic and hydrophobic neutral organic chemicals described by Undeman et al.,[81] volatilization becomes a potential source of leaf contamination through the soil–air pathway.[82]

4.1 Root Uptake

The chemical speciation of the tested EOCs can be anticipated from their pKa (Table 1) and the pH of the soil (6.42). Whereas BPA, CAF, CBZ, SMT, TCS, and TON occur predominantly in neutral forms, IBU is predominantly anionic, and PROP is cationic. Accordingly, the low concentration of IBU in the roots (Table 2) could be explained by its electronegativity, as long as the root membranes have a negatively charged potential[83] (i.e. plasmalemma), which would hinder the absorption of negatively charged ions. Instead, PROP (a positively charged compound, Table 1) occurred in the root at a higher concentration than IBU, but at a lower concentration than most of the neutral products (Figure 1B).

CBZ was the product found in the highest concentrations in the roots. This could be explained by its neutrality and low hydrophobicity (log $D_{\mathrm{OW}} = 2.25$). Indeed, it has been established that neutral products with log K_{OW} between 1 and 3 can be readily absorbed by the roots because they exhibit a high root membrane permeability. In addition, they exhibit a low interaction with the soil's organic colloids.[25] However, since the soil we used had a low CEC, more hydrophobic products (log $K_{\mathrm{OW}} > 4.66$) could also be easily sorbed by roots. This is the case of TCS and TON. Besides, highly hydrophilic neutral products, such as CAF and SMT (log $D_{\mathrm{OW}} < 0.85$), showed an appreciable root uptake, although less than CBZ, TCS, and TON.

The high concentration of CBZ found in roots is consistent with the literature. For example, in a study of soybean plants irrigated with 10 μg L^{-1} of CBZ and TCS, Wu et al.[9] reported that TCS was found mostly in the roots (16.9 ± 2.6 ng g^{-1} dw). In this study, TCS likewise exhibited a higher concentration in the roots (147 ± 92 ng g^{-1} dw), while CBZ was found mostly in the leaves (216 ± 75 ng g^{-1} dw). Shenker et al.[80] irrigated cucumbers with fresh and reclaimed water spiked with 1 μg L^{-1} of CBZ. The CBZ concentration found in the roots was between 2 and 4.5 μg g^{-1} in fw, while the concentration in the leaves ranged from 19 to 39 μg g^{-1}. Wu et al.[12] reported that several PPCPs were detected in edible parts of common vegetables that had been watered with PPCP-spiked treated wastewater. CBZ concentrations of between 0.1 and 2.5 ng g^{-1}, depending on the plant species, were detected in lettuce, celeries, cabbages, cucumbers, bell peppers, and tomatoes, although the initial concentrations were lower than in this study. Interestingly, like most of the compounds examined here, the PPCPs were found at higher concentrations in the roots than in the leaves. Goldstein et al.[15]

reported CBZ levels between 50 and 500 ng g^{-1} dw in cucumbers and tomatoes. CAF was detected at concentrations between 1 and 9 ng g^{-1} dw in the same plants. Hence, although this experiment used a simplified set-up and a low CEC soil, the findings are comparable to those of other studies performed with real soil.

4.2 Biodegradability

Biodegradation of EOCs in the rhizosphere is considered to be the most significant removal mechanism for EOCs that are not readily absorbed by the roots. Indeed, as much as 40% of a plant's photosynthate can be released into the soil as sugars, organic acids, and larger organic compounds such as root exudates.[84] These exudates are used as carbon and energy sources by soil microbial biomass, leading to a significant enrichment compared with soil that is uninfluenced by roots.[85] Several studies have addressed the dissipation of pharmaceuticals in agricultural soil, but the interaction between soil and the rhizosphere effect has been neglected.[86, 87] This notwithstanding, it is widely accepted that, in phytoremediation, the rhizosphere plays a role in removing organic contaminants from soil through a synergistic interaction of many factors.[29] The results of this study underscore the importance of the relative persistence of EOCs in the rhizosphere as a key primary parameter for assessing plants' exposure to them.

TCS is the only tested EOC with a positive concentration factor in the soil near the roots (S_RCF). This accumulation is consistent with the recalcitrance resulting from its biocidal activity. Interestingly, IBU was spiked as a racemic mixture; however, an EF of 0.74 was found in the soil. Furthermore, an EF of 0.69 was observed in the roots. This could indicate biotic degradation in both the rhizosphere and the roots. However, the EF was 0.50 in the leaves. Therefore, racemization was taking place inside the plant. This can be explained by different detoxification processes that occur in plants. For instance, plants have their own detoxification system with many enzymes that can metabolize organic contaminants (e.g., cytochrome P450, monooxygenases, peroxidases, glutathione S-transferases), and endophytic bacteria can live inside plants and have a potentially large impact on their metabolism.[32, 88] The total degradation of both plant and bacteria could lead to a racemization of the IBU in the leaves. Deeper research in the field of degradation routes in soil and plants is needed.

4.3 Modeling Plant Uptake

The relationship between EOC concentration in soil and plant uptake has seldom been studied. Usually, root concentration factors (R_{CF}) are calculated based on their nominal concentrations; however, as demonstrated in the previous section, their behavior in the rhizosphere is largely dependent on the compound. One of the few existing studies used a simplified two-compartment model[89] to assess the plant concentration and found a linear relationship between soil-water concentration and plant concentration. However, that model was only validated for norfloxacin. Kumar et al.[90] observed an increase of chlortetracycline in onions and cabbage related to the dose of manure applied to the soil.

However, to the best of our knowledge, this is the first study to report a linear relationship between root and leaf concentrations for a wide range of EOCs supplied in irrigation water. Moreover, the fact that the leaf translocation concentration factors (L_{TCF_i}) remain fairly stable regardless of the dose of EOC applied (Fig. 3C) makes it possible to predict fairly accurately the content of the tested EOC based on the dose supplied and the calculated average soil concentration (Fig. 5).

Although the experimental setup used in this study was rather simple (low CEC, no leachates produced), the approach could be particularly useful in risk assessment studies for estimating EOC concentrations in crops in the worst case scenario, in which the soil-contaminant interaction is negligible.

5. Conclusions

- Although previous studies in real scenarios have shown that several organic pollutants can be taken up by plants, it is difficult, if not impossible to reproduce the experimental set-up elsewhere. In this study, a mesocosm characterized by a low CEC exhibited similar behavior with regard to the evaluated EOCs as in previous studies. Degradation, uptake and translocation processes were all highly dependent on the specific EOC evaluated and the compartment.
- Linear relationships observed between the root concentration and the application dose, along with the stability of the leaf translocation concentration factors, makes it possible to predict the leaf concentrations of tested EOCs fairly accurately.
- Enantiomeric IBU degradation was detected in the soil, and a racemization trend was observed in the plants, from the roots to the leaves. This would seem to suggest that mixed biotic degradation pathways might occur in the plant either through endophytic bacteria or the plant's own detoxification system, leading to complete racemization in the leaves. Further research is required to address the complexity of the biotic degradation pathways for EOCs in plants.

Annex I

Definition of symbols used in the article

b_{R_C/S_C}	Linear regression coefficient of R_{C_i} over S_{C_i} over the course of the different treatments *i*
IW_{C_i}	Calculated average irrigation water concentration of a given EOC in treatment *i*
L_{C_i}	Leaf concentration of a given EOC in treatment *i*
L'_{C_i}	Predicted leaf concentration of a given EOC in treatment *i* (Eq. 5)
L_{SC}	Standardized leaf concentration of a given EOC (Eq. 1)
L_{TCF_i}	Leaf translocation factor of a given EOC in treatment *i* (Eq. 5)
L_{TCF_m}	Mean leaf translocation factor of a given EOC
R_{C_i}	Root concentration of a given EOC in treatment *i*
R_{CF_i}	Root concentration factor of a given EOC in treatment *i* (Eq. 4)
R_{SC}	Standardized root concentration of a given EOC (Eq. 1)
S_{C_i}	Calculated average soil concentration of a given EOC in treatment *i*
SR_{C_i}	Concentration in the soil close to the roots of a given EOC in treatment *i*
SR_{SC}	Standardized concentration in the soil close to the roots of a given EOC (Eq. 1)
SR_{CF_i}	Concentration factor in the soil close to the roots of a given EOC in treatment *i* (Eq. 3)

ASSOCIATED CONTENT

Supporting Information

Chemicals; analysis of soil, roots, and leaves (Table S1 and Table S2); limits of detection and quantification (Table S3); recoveries of surrogates in all samples (Table S4); linear regression coefficients (Table S5). This material is available online free of charge at http://pub.acs.org/

AUTHOR INFORMATION

Corresponding author

Phone: +34 934006119, e-mail: jbtqam@cid.csic.es

ACKOWLEDGEMENTS

Authors thank to the Spanish Ministry of Economy and Competitiveness (MINECO) for funding (CGL2011-24844). C.H. acknowledges a predoctoral fellowship (BES-2012-055067) from MINECO. Technical assistance in the Agropolis-UPC and mass spectrometry facility provided by Mr. M Massip and Dr. R. Chaler and Ms. D. Fanjul respectively is kindly appreciated.

REFERENCES

[1] P. Gerland, A.E. Raftery, H. Ševčíková, N. Li, D. Gu, T. Spoorenberg, L. Alkema, B.K. Fosdick, J. Chunn, N. Lalic, G. Bay, T. Buettner, G.K. Heilig, J. Wilmoth, World population stabilization unlikely this century, Science 346 (2014) 234-237.

[2] V.G. Karen Frenken, Irrigation Water Requirement and Water Withdrawal by Country, in, 2012.

[3] D. Calderón-Preciado, V. Matamoros, J.M. Bayona, Occurrence and potential crop uptake of emerging contaminants and related compounds in an agricultural irrigation network, Sci. Total Environ. 412–413 (2011) 14-19.

[4] K. Kümmerer, Antibiotics in the aquatic environment – A review – Part I, Chemosphere 75 (2009) 417-434.

[5] Handbook of Phytoremediation, Nova Science, 2011.

[6] P.A. Herklotz, P. Gurung, B. Vanden Heuvel, C.A. Kinney, Uptake of human pharmaceuticals by plants grown under hydroponic conditions, Chemosphere 78 (2010) 1416-1421.

[7] D. Calderón-Preciado, Q. Renault, V. Matamoros, N. Cañameras, J.M. Bayona, Uptake of Organic Emergent Contaminants in Spath and Lettuce: An In Vitro Experiment, J. Agric. Food. Chem. 60 (2012) 2000-2007.

[8] A. Zhang, W. Luo, J. Sun, H. Xiao, W. Liu, Distribution and uptake pathways of organochlorine pesticides in greenhouse and conventional vegetables, Sci. Total Environ.

[9] C. Wu, A.L. Spongberg, J.D. Witter, M. Fang, K.P. Czajkowski, Uptake of pharmaceutical and personal care products by soybean plants from soils applied with biosolids and irrigated with contaminated water, Environ. Sci. Technol. 44 (2010) 6157-6161.

[10] D. Calderón-Preciado, V. Matamoros, R. Savé, P. Muñoz, C. Biel, J.M. Bayona, Uptake of microcontaminants by crops irrigated with reclaimed water and groundwater under real field greenhouse conditions, Environ. Sci. Pollut. R. 20 (2013) 3629-3638.

[11] A. Macherius, T. Eggen, W.G. Lorenz, T. Reemtsma, U. Winkler, M. Moeder, Uptake of Galaxolide, Tonalide, and Triclosan by Carrot, Barley, and Meadow Fescue Plants, J. Agric. Food. Chem. 60 (2012) 7785-7791.

[12] X. Wu, J.L. Conkle, F. Ernst, J. Gan, Treated Wastewater Irrigation: Uptake of Pharmaceutical and Personal Care Products by Common Vegetables under Field Conditions, Environ. Sci. Technol. 48 (2014) 11286-11293.

[13] D. Calderón-Preciado, C. Jiménez-Cartagena, V. Matamoros, J.M. Bayona, Screening of 47 organic microcontaminants in agricultural irrigation waters and their soil loading, Water Res. 45 (2011) 221-231.

[14] M. Marsoni, F. De Mattia, M. Labra, A. Bruno, M. Bracale, C. Vannini, Uptake and effects of a mixture of widely used therapeutic drugs in Eruca sativa L. and Zea mays L. plants, Ecotox. Environ. Safe. 108 (2014) 52-57.

[15] M. Goldstein, M. Shenker, B. Chefetz, Insights into the Uptake Processes of Wastewater-Borne Pharmaceuticals by Vegetables, Environ. Sci. Technol. 48 (2014) 5593-5600.

[16] C.N. Legind, A. Rein, J. Serre, V. Brochier, C.-S. Haudin, P. Cambier, S. Houot, S. Trapp, Simultaneous Simulations of Uptake in Plants and Leaching to Groundwater of Cadmium and Lead for Arable Land Amended with Compost or Farmyard Manure, PLoS ONE 7 (2012) e47002.

[17] N.T. Dinh, D.T. Vu, D. Mulligan, A.V. Nguyen, Accumulation and distribution of zinc in the leaves and roots of the hyperaccumulator Noccaea caerulescens, Environ. Exp. Bot. 110 (2015) 85-95.

[18] T. Nishikiori, M. Watanabe, M.K. Koshikawa, T. Takamatsu, Y. Ishii, S. Ito, A. Takenaka, K. Watanabe, S. Hayashi, Uptake and translocation of radiocesium in cedar leaves following the Fukushima nuclear accident, Sci. Total Environ. 502 (2015) 611-616.

[19] E. Terzaghi, G. Zacchello, M. Scacchi, G. Raspa, K.C. Jones, B. Cerabolini, A. Di Guardo, Towards more ecologically realistic scenarios of plant uptake modelling for chemicals: PAHs in a small forest, Sci. Total Environ. 505 (2015) 329-337.

[20] S. Trapp, T. Eggen, Simulation of the plant uptake of organophosphates and other emerging pollutants for greenhouse experiments and field conditions, Environ. Sci. Pollut. R. 20 (2013) 4018-4029.

[21] R.S. Prosser, S. Trapp, P.K. Sibley, Modeling Uptake of Selected Pharmaceuticals and Personal Care Products into Food Crops from Biosolids-Amended Soil, Environ. Sci. Technol. 48 (2014) 11397-11404.

[22] C.N. Legind, C.M. Kennedy, A. Rein, N. Snyder, S. Trapp, Dynamic plant uptake model applied for drip irrigation of an insecticide to pepper fruit plants, Pest. Manag. Sci. 67 (2011) 521-527.

[23] A. Rein, C.N. Legind, S. Trapp, New concepts for dynamic plant uptake models, SAR QSAR Environ. Res. 22 (2011) 191-215.

[24] S. Trapp, Calibration of a Plant Uptake Model with Plant- and Site-Specific Data for Uptake of Chlorinated Organic Compounds into Radish, Environ. Sci. Technol. 49 (2015) 395-402.

[25] G.G. Briggs, R.H. Bromilow, A.A. Evans, Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley, Pestic. Sci. 13 (1982) 495-504.

[26] G.G. Briggs, R.L.O. Rigitano, R.H. Bromilow, Physico-chemical factors affecting uptake by roots and translocation to shoots of weak acids in barley, Pestic. Sci. 19 (1987) 101-112.

[27] R.H. Bromilow, K. Chamberlain, Principles governing uptake and transport of chemicals, in: S.M.F. Trapp, J.C. (Ed.) Plant Contamination: Modeling and Simulation of Organic Chemical Processes, Lewis/CRC Press, Boca Raton, FL, USA, 1995, pp. 37-68.

[28] S. Trapp, Plant uptake and transport models for neutral and ionic chemicals, Environ. Sci. Pollut. R. 11 (2004) 33-39.

[29] K.E. Gerhardt, X.-D. Huang, B.R. Glick, B.M. Greenberg, Phytoremediation and rhizoremediation of organic soil contaminants: Potential and challenges, Plant Sci. 176 (2009) 20-30.

[30] C. Lodewyckx, J. Vangronsveld, F. Porteous, E.R. Moore, S. Taghavi, M. Mezgeay, D.v. der Lelie, Endophytic bacteria and their potential applications, Crit. Rev. Plant Sci. 21 (2002) 583-606.

[31] T. Barac, S. Taghavi, B. Borremans, A. Provoost, L. Oeyen, J.V. Colpaert, J. Vangronsveld, D. van der Lelie, Engineered endophytic bacteria improve phytoremediation of water-soluble, volatile, organic pollutants, Nat. Biotechnol. 22 (2004) 583-588.

[32] A. Sauvetre, P. Schröder, Uptake of Carbamazepine by rhizomes and endophytic bacteria of Phragmites australis, Front. Plant Sci. 6 (2015).

[33] M. Afzal, Q.M. Khan, A. Sessitsch, Endophytic bacteria: Prospects and applications for the phytoremediation of organic pollutants, Chemosphere 117 (2014) 232-242.

[34] J.W. Kang, Z. Khan, S.L. Doty, Biodegradation of Trichloroethylene by an Endophyte of Hybrid Poplar, Appl. Environ. Microb. 78 (2012) 3504-3507.

[35] K.J. Germaine, X. Liu, G.G. Cabellos, J.P. Hogan, D. Ryan, D.N. Dowling, Bacterial endophyte-enhanced phytoremediation of the organochlorine herbicide 2,4-dichlorophenoxyacetic acid, FEMS Microbiol. Ecol. 57 (2006) 302-310.

[36] Y. Qi, D. Liu, M. Sun, S. Di, P. Wang, Z. Zhou, The Chiral Separation and Enantioselective Degradation of the Chiral Herbicide Napropamide, Chirality 26 (2014) 108-113.

[37] H. Fromme, T. Küchler, T. Otto, K. Pilz, J. Müller, A. Wenzel, Occurrence of phthalates and bisphenol A and F in the environment, Water Res. 36 (2002) 1429-1438.

[38] A. Belfroid, M. van Velzen, B. van der Horst, D. Vethaak, Occurrence of bisphenol A in surface water and uptake in fish: evaluation of field measurements, Chemosphere 49 (2002) 97-103.

[39] A. Careghini, A. Mastorgio, S. Saponaro, E. Sezenna, Bisphenol A, nonylphenols, benzophenones, and benzotriazoles in soils, groundwater, surface water, sediments, and food: a review, Environ. Sci. Pollut. R. 22 (2015) 5711-5741.

[40] N. Benachour, A. Aris, Toxic effects of low doses of Bisphenol-A on human placental cells, Toxicol. Appl. Pharmacol. 241 (2009) 322-328.

[41] H. Yamamoto, Y. Nakamura, S. Moriguchi, Y. Nakamura, Y. Honda, I. Tamura, Y. Hirata, A. Hayashi, J. Sekizawa, Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments, Water Res. 43 (2009) 351-362.

[42] A. Bahlmann, W. Brack, R.J. Schneider, M. Krauss, Carbamazepine and its metabolites in wastewater: Analytical pitfalls and occurrence in Germany and Portugal, Water Res. 57 (2014) 104-114.

[43] A. Jurado, R. López-Serna, E. Vázquez-Suné, J. Carrera, E. Pujades, M. Petrovic, D. Barceló, Occurrence of carbamazepine and five metabolites in an urban aquifer, Chemosphere 115 (2014) 47-53.

[44] J. Maszkowska, S. Stolte, J. Kumirska, P. Łukaszewicz, K. Mioduszewska, A. Puckowski, M. Caban, M. Wagil, P. Stepnowski, A. Białk-Bielin´ska, Beta-blockers in the environment: Part I. Mobility and hydrolysis study, Sci. Total Environ. 493 (2014) 1112-1121.

[45] J. Maszkowska, S. Stolte, J. Kumirska, P. Łukaszewicz, K. Mioduszewska, A. Puckowski, M. Caban, M. Wagil, P. Stepnowski, A. Białk-Bielińska, Beta-blockers in the environment: Part II. Ecotoxicity study, Sci. Total Environ. 493 (2014) 1122-1126.

[46] D.B. Huggett, B.W. Brooks, B. Peterson, C.M. Foran, D. Schlenk, Toxicity of select beta adrenergic receptor-blocking pharmaceuticals (B-blockers) on aquatic organisms, Arch. Environ. Contam. Toxicol. 43 (2002) 229-235.

[47] M. Wang, C. Peng, W. Chen, B. Markert, Ecological risks of polycyclic musk in soils irrigated with reclaimed municipal wastewater, Ecotox. Environ. Safe. 97 (2013) 242-247.

[48] F. Balk, R.A. Ford, Environmental risk assessment for the polycyclic musks AHTN and HHCB in the EU: I. Fate and exposure assessment, Toxicol. Lett. 111 (1999) 57-79.

[49] J. Yin, H. Wang, J. Zhang, N. Zhou, F. Gao, Y. Wu, J. Xiang, B. Shao, The occurrence of synthetic musks in human breast milk in Sichuan, China, Chemosphere 87 (2012) 1018-1023.

[50] C.S. Kang, J.-H. Lee, S.-K. Kim, K.-T. Lee, J.S. Lee, P.S. Park, S.H. Yun, K. Kannan, Y.W. Yoo, J.Y. Ha, S.W. Lee, Polybrominated diphenyl ethers and synthetic

musks in umbilical cord Serum, maternal serum, and breast milk from Seoul, South Korea, Chemosphere 80 (2010) 116-122.

[51] M. Parolini, S. Magni, I. Traversi, S. Villa, A. Finizio, A. Binelli, Environmentally relevant concentrations of galaxolide (HHCB) and tonalide (AHTN) induced oxidative and genetic damage in Dreissena polymorpha, J. Hazard. Mater. 285 (2015) 1-10.

[52] S. Wegst-Uhrich, D. Navarro, L. Zimmerman, D. Aga, Assessing antibiotic sorption in soil: a literature review and new case studies on sulfonamides and macrolides, Chemistry Central Journal 8 (2014) 5.

[53] L.A. Poirier, D.R. Doerge, D.W. Gaylor, M.A. Miller, R.J. Lorentzen, D.A. Casciano, F.F. Kadlubar, B.A. Schwetz, An FDA review of sulfamethazine toxicity, Regul. Toxicol. Pharmacol. 30 (1999) 217-222.

[54] A. Pruden, R. Pei, H. Storteboom, K.H. Carlson, Antibiotic Resistance Genes as Emerging Contaminants: Studies in Northern Colorado, Environ. Sci. Technol. 40 (2006) 7445-7450.

[55] D. Ou, B. Chen, R. Bai, P. Song, H. Lin, Contamination of sulfonamide antibiotics and sulfamethazine-resistant bacteria in the downstream and estuarine areas of Jiulong River in Southeast China, Environ. Sci. Pollut. R. (2015) 1-10.

[56] A.B.A. Boxall, D.W. Kolpin, B. Halling-Sørensen, J. Tolls, Peer Reviewed: Are Veterinary Medicines Causing Environmental Risks?, Environ. Sci. Technol. 37 (2003) 286A-294A.

[57] Triclosan: environmental exposure, toxicity and mechanisms of action, J. Appl. Toxicol. 31 (2011) 285-311.

[58] H. Singer, S. Müller, C. Tixier, L. Pillonel, Triclosan: Occurrence and Fate of a Widely Used Biocide in the Aquatic Environment: Field Measurements in Wastewater

Treatment Plants, Surface Waters, and Lake Sediments, Environ. Sci. Technol. 36 (2002) 4998-5004.

[59] G. Bedoux, B. Roig, O. Thomas, V. Dupont, B. Le Bot, Occurrence and toxicity of antimicrobial triclosan and by-products in the environment, Environ. Sci. Pollut. R. 19 (2012) 1044-1065.

[60] C.A. Giuliano, M.J. Rybak, Efficacy of Triclosan as an Antimicrobial Hand Soap and Its Potential Impact on Antimicrobial Resistance: A Focused Review, Pharmacotherapy 35 (2015) 328-336.

[61] B. Thomas, A. Ali, G. Bella de la, O.K. Bi, U.H. Rolf, Fate of Caffeine in the Environment and Ecotoxicological Considerations, in: Contaminants of Emerging Concern in the Environment: Ecological and Human Health Considerations, American Chemical Society, 2010, pp. 257-273.

[62] Z. Rodriguez del Rey, E.F. Granek, S. Sylvester, Occurrence and concentration of caffeine in Oregon coastal waters, Mar. Pollut. Bull. 64 (2012) 1417-1424.

[63] J.E. James, Dietary caffeine: "Unnatural" exposure requiring precaution?, J. Subst. Use 19 (2014) 394-397.

[64] N.N.G. Letić, M.L. Milanović, N.B. Milić, M.B.V. Miloradov, J.R. Radonić, I.J. Mihajlović, M.M.T. Sekulić, Determination of Emerging Substances in the Danube and Potential Risk Evaluation, Clean - Soil, Air, Water 43 (2015) 731-738.

[65] O.A.H. Jones, N. Voulvoulis, J.N. Lester, Aquatic environmental assessment of the top 25 English prescription pharmaceuticals, Water Res. 36 (2002) 5013-5022.

[66] H.-R. Buser, T. Poiger, M.D. Müller, Occurrence and Environmental Behavior of the Chiral Pharmaceutical Drug Ibuprofen in Surface Waters and in Wastewater, Environ. Sci. Technol. 33 (1999) 2529-2535.

[67] C. Tixier, H.P. Singer, S. Oellers, S.R. Müller, Occurrence and Fate of Carbamazepine, Clofibric Acid, Diclofenac, Ibuprofen, Ketoprofen, and Naproxen in Surface Waters, Environ. Sci. Technol. 37 (2003) 1061-1068.

[68] B. Petrie, R. Barden, B. Kasprzyk-Hordern, A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring, Water Res. 72 (2015) 3-27.

[69] D.R. Hoagland, D.I. Arnon, The water-culture method for growing plants without soil, Circular. California Agricultural Experiment Station 347 (1950) 1-32.

[70] D. Calderón-Preciado, C. Jiménez-Cartagena, G. Peñuela, J. Bayona, Development of an analytical procedure for the determination of emerging and priority organic pollutants in leafy vegetables by pressurized solvent extraction followed by GC–MS determination, Anal. Bioanal. Chem. 394 (2009) 1319-1327.

[71] N.H. Hashim, S.J. Khan, Enantioselective analysis of ibuprofen, ketoprofen and naproxen in wastewater and environmental water samples, J. Chromatogr. A 1218 (2011) 4746-4754.

[72] N.H. Hashim, S. Shafie, S.J. Khan, Enantiomeric fraction as an indicator of pharmaceutical biotransformation during wastewater treatment and in the environment – a review, Environ. Technol. 31 (2010) 1349-1370.

[73] T. Harner, K. Wiberg, R. Norstrom, Enantiomer Fractions Are Preferred to Enantiomer Ratios for Describing Chiral Signatures in Environmental Analysis, Environ. Sci. Technol. 34 (2000) 218-220.

[74] R Development Core Team, R: A language and environment for statistical computing, in, R Foundation for Statistical Computing, Viena, Austria, 2015.

[75] D. Shargil, Z. Gerstl, P. Fine, I. Nitsan, D. Kurtzman, Impact of biosolids and wastewater effluent application to agricultural land on steroidal hormone content in lettuce plants, Sci. Total Environ. 505 (2015) 357-366.

[76] C. Wu, A.L. Spongberg, J.D. Witter, B.B.M. Sridhar, Transfer of wastewater associated pharmaceuticals and personal care products to crop plants from biosolids treated soil, Ecotox. Environ. Safe. 85 (2012) 104-109.

[77] C.S. Holling, J.L. Bailey, B. Vanden Heuvel, C.A. Kinney, Uptake of human pharmaceuticals and personal care products by cabbage (Brassica campestris) from fortified and biosolids-amended soils, J. Environ. Monit. 14 (2012) 3029-3036.

[78] L. Sabourin, P. Duenk, S. Bonte-Gelok, M. Payne, D.R. Lapen, E. Topp, Uptake of pharmaceuticals, hormones and parabens into vegetables grown in soil fertilized with municipal biosolids, Sci. Total Environ. 431 (2012) 233-236.

[79] T. Malchi, Y. Maor, G. Tadmor, M. Shenker, B. Chefetz, Irrigation of root vegetables with treated wastewater: Evaluating uptake of pharmaceuticals and the associated human health risks, Environ. Sci. Technol. 48 (2014) 9325-9333.

[80] M. Shenker, D. Harush, J. Ben-Ari, B. Chefetz, Uptake of carbamazepine by cucumber plants – A case study related to irrigation with reclaimed wastewater, Chemosphere 82 (2011) 905-910.

[81] E. Undeman, G. Czub, M.S. McLachlan, Addressing temporal variability when modeling bioaccumulation in plants, Environ. Sci. Technol. 43 (2009) 3751-3756.

[82] C.D. Collins, E. Finnegan, Modeling the Plant Uptake of Organic Chemicals, Including the Soil−Air−Plant Pathway, Environ. Sci. Technol. 44 (2010) 998-1003.

[83] H.Z. P. Sitte, F. Ehrendorfer, A. Bresinsky, E. Strasburger, F. Noll, H. Schenck, Lehrbuch der Botanik für Hochschulen, 33 ed., Gustav Fischer Verlag, Stuttgart, Germany, 1991.

[84] M.B. Leigh, J.S. Fletcher, X. Fu, F.J. Schmitz, Root turnover: an important source of microbial substrates in rhizosphere remediation of recalcitrant contaminants, Environ. Sci. Technol. 36 (2002) 1579-1583.

[85] Q. Chaudhry, M. Blom-Zandstra, S. Gupta, E.J. Joner, Utilising the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment, Environ. Sci. Pollut. R. Int. 12 (2005) 34-48.

[86] A. Grossberger, Y. Hadar, T. Borch, B. Chefetz, Biodegradability of pharmaceutical compounds in agricultural soils irrigated with treated wastewater, Environ. Pollut. 185 (2014) 168-177.

[87] P. Dalkmann, C. Siebe, W. Amelung, M. Schloter, J. Siemens, Does Long-Term Irrigation with Untreated Wastewater Accelerate the Dissipation of Pharmaceuticals in Soil?, Environ. Sci. Technol. 48 (2014) 4963-4970.

[88] G. Brader, S. Compant, B. Mitter, F. Trognitz, A. Sessitsch, Metabolic potential of endophytic bacteria, Curr. Opin. Biotechnol. 27 (2014) 30-37.

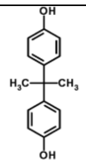
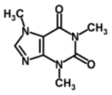
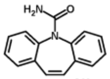
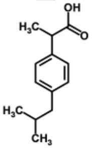
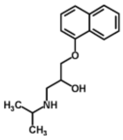
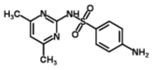
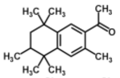
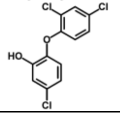
[89] R. Cropp, D. Hawker, M. Boonsaner, Predicting the Accumulation of Organic Contaminants from Soil by Plants, Bull. Environ. Contam. Toxicol. 85 (2010) 525-529.

[90] K. Kumar, S.C. Gupta, S.K. Baidoo, Y. Chander, C.J. Rosen, Antibiotic uptake by plants from soil fertilized with animal manure, J. Environ. Qual. 34 (2005) 2082-2085.

[91] S. Trapp, Bioaccumulation of Polar and Ionizable Compounds in Plants, in: J. Devillers (Ed.) Ecotoxicology Modeling, Springer US, 2009, pp. 299-353.

TABLES

Table 1. Physicochemical properties of the selected emerging organic contaminants.

Name	Molecular structure	pKa[1]	Solubility (mg L^{-1})	Log K_{OW}[2]	Log K_{OA}[2]	Log K_{AW}[2]	f_n[3]
Bisphenol A (BPA)		8.7[0/-]	173	3.32	12.75	-9.43	0.995
Caffeine (CAF)		0.8[+/0]	2632	-0.07	8.77	-8.83	0.999
Carbamazepine (CBZ)		2.45[+/0]	17.7	2.45	10.81	-7.20	0.999
Ibuprofen (IBU)		4.3[0/-]	41.1	3.97	9.18	-5.21	0.008
Propranolol (PROP)		9.5[+/0]	228	3.48	13.97	-10.49	0.001
Sulfamethazine (SMT)		2.7[+/0] 7.4[0/-]	2846	0.89	8.29	-8.10	0.797
Tonalide (TON)		NA[4]	0.29	5.70	7.95	-2.04	1.000
Triclosan (TCS)		7.9[0/-]	4.62	4.76	11.45	-4.08	0.967

[1] Dissociation reaction, [0]: neutral; [+]: cationic; [-]: anionic.

[2] Log K_{OW}, Log K_{OA} and Log K_{AW} from database provided by Episuite v4.11 (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm)

[3] The neutral fraction f_n was calculated from Trapp et al.[91] at soil pH 6.42 .

[4] Not applicable

Table 2. Mean concentration (N = 4. ± sd; soil in ng g^{-1}; root in ng g^{-1} dw; leaf: ng g^{-1} dw) of the emerging organic contaminants in the different compartments at the end of the exposure experiment (70 d)

Compound	Compartment	Applied concentration μg kg^{-1}				
		0	11.7	29.2	58.3	116.7
BPA	**Soil**	< LOD	5.1 ± 3.5	11 ± 3	25 ± 3	55 ± 16
	Root	< LOD	73 ± 11	124 ± 18	212 ± 71	325 ± 69
	Leaf	< LOD	33 ± 17	54 ± 8	83 ± 19	158 ± 53
CAF	**Soil**	1.5 ± 0.9	4.2 ± 1.0	5.8 ± 0.6	18 ± 6	64 ± 10
	Root	< LOD	32 ± 9	126 ± 50	255 ± 61	398 ± 105
	Leaf	< LOD	32 ± 6	53 ± 11	77 ± 8	147 ± 20
CBZ	**Soil**	< LOD	0.85 ± 0.91	10.4 ± 10	37 ± 4	117 ± 30
	Root	< LOD	142 ± 88	234 ± 98	473 ± 116	1214 ± 314
	Leaf	< LOD	233 ± 47	461 ± 48	1031 ± 149	2054 ± 315
IBU	**Soil**	< LOD	0.73 ± 0.22	2.1 ± 0.81	8.7 ± 3.4	24 ± 3
	Root	< LOD	< LOD	13 ± 5	69 ± 32	223 ± 68
	Leaf	< LOD	0.93 ± 0.32	2.4 ± 1	4.9 ± 1.1	24 ± 7
PROP	**Soil**	< LOD	1.5 ± 0.2	3.8 ± 1.7	9.7 ± 6.9	27 ± 18
	Root	< LOD	113 ± 14	195 ± 60	313 ± 49	393 ± 47
	Leaf	< LOD	< LOD	29 ± 8	67 ± 11	119 ± 26
SMT	**Soil**	< LOD	0.30 ± 0.11	0.82 ± 0.44	2.4 ± 0.9	4.7 ± 1.9
	Root	< LOD	60 ± 18	92 ± 22	243 ± 54	495 ± 64
	Leaf	< LOD	< LOD	< LOD	< LOD	< LOD
TON	**Soil**	1.5 ± 1.1	5.3 ± 1.8	13 ± 3	21 ± 14	39 ± 12
	Root	< LOD	9.4 ± 4.3	117 ± 27	270 ± 69	587 ± 122
	Leaf	< LOD	26 ± 14	73 ± 6	105 ± 19	321 ± 99
TCS	**Soil**	1.2 ± 1.0	10 ± 4	56 ± 18	97 ± 25	167 ± 32
	Root	< LOD	21 ± 18	147 ± 92	353 ± 95	772 ± 206
	Leaf	< LOD	13 ± 2	17 ± 1	25 ± 3	32 ± 3

FIGURE CAPTIONS

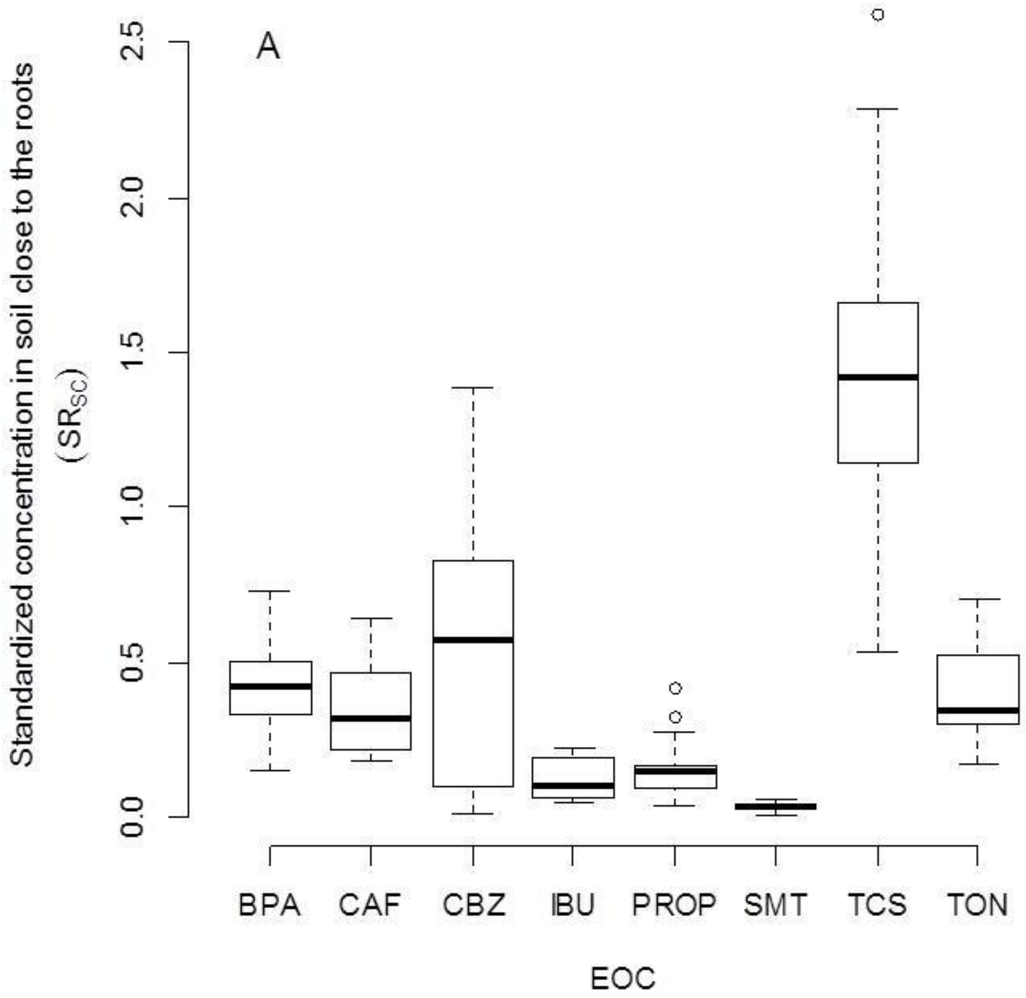
Figure 1. Boxplots of standarized concentration of tested EOCs in the three different analyzed compartments (a) in the soil close to the roots (SR_{SC}), (b) in the roots (R_{SC}) and (c) in the leaves (L_{SC}).

Figure 2. Boxplots of the enantiomeric factors (EF) of IBU in the soil close to the roots, in the roots and in the leaves. The horizontal line was the value of the commercial raceminc mixture of IBU (EF = 0.50).

Figure 3. Mean of the concentration factors (a) in the soil close to the roots (SR_{CF}), (b) in the roots (R_{CF}) and (c) and leaf translocation factor (L_{TCF}) along the initial applied concentration in soil (S_C).

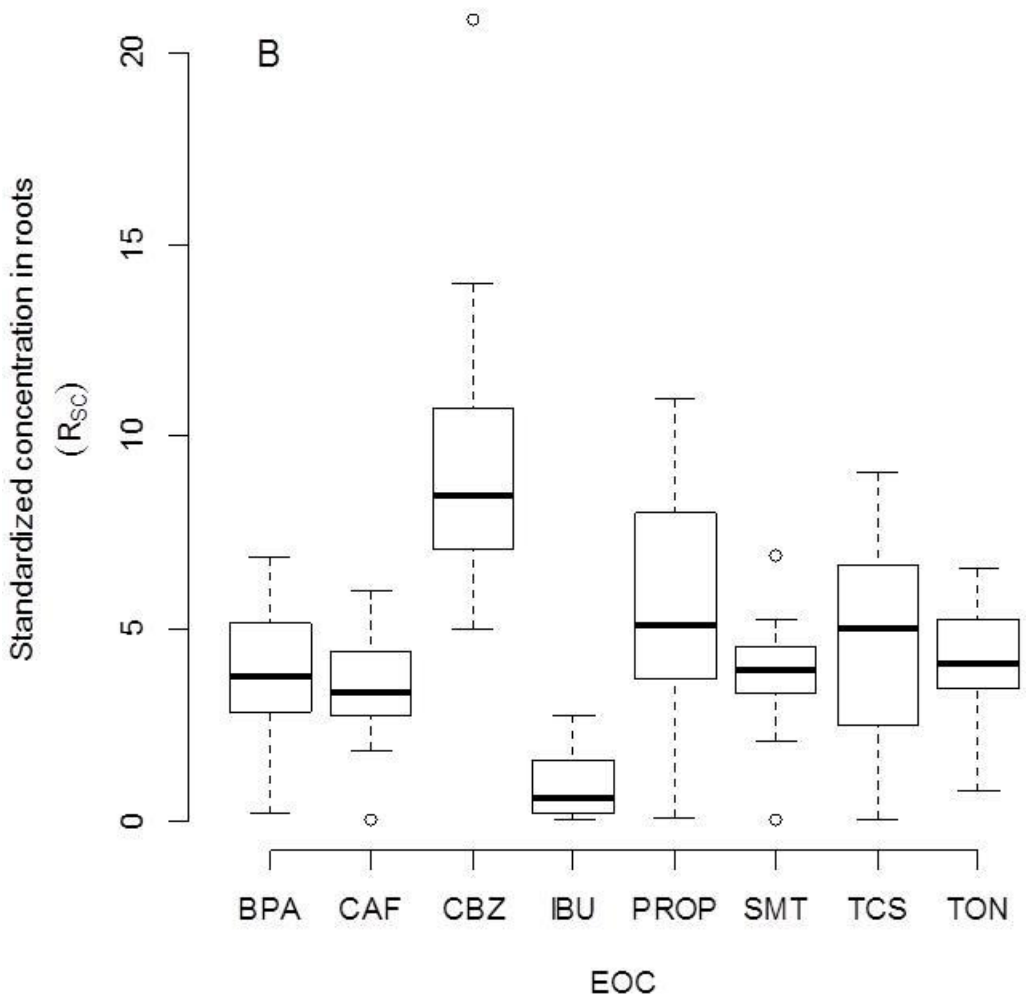
Figure 4. Concentration of tested EOC in the roots (R_C, ng g^{-1} dw) over application rate expressed as the average concentration in the soil (S_C, µg kg^{-1} dw)

Figure 5. Values of tested EOC in the leaves compared with the values obtained from the product of the concentration of supplied EOC in the soil (S_C), the concentration factor of the roots (R_{CF}) and leaf translocation concentration factor (L_{TCF}) (Equation 2).



762

763 **Figure 1A.**



764

765 **Figure 1B.**

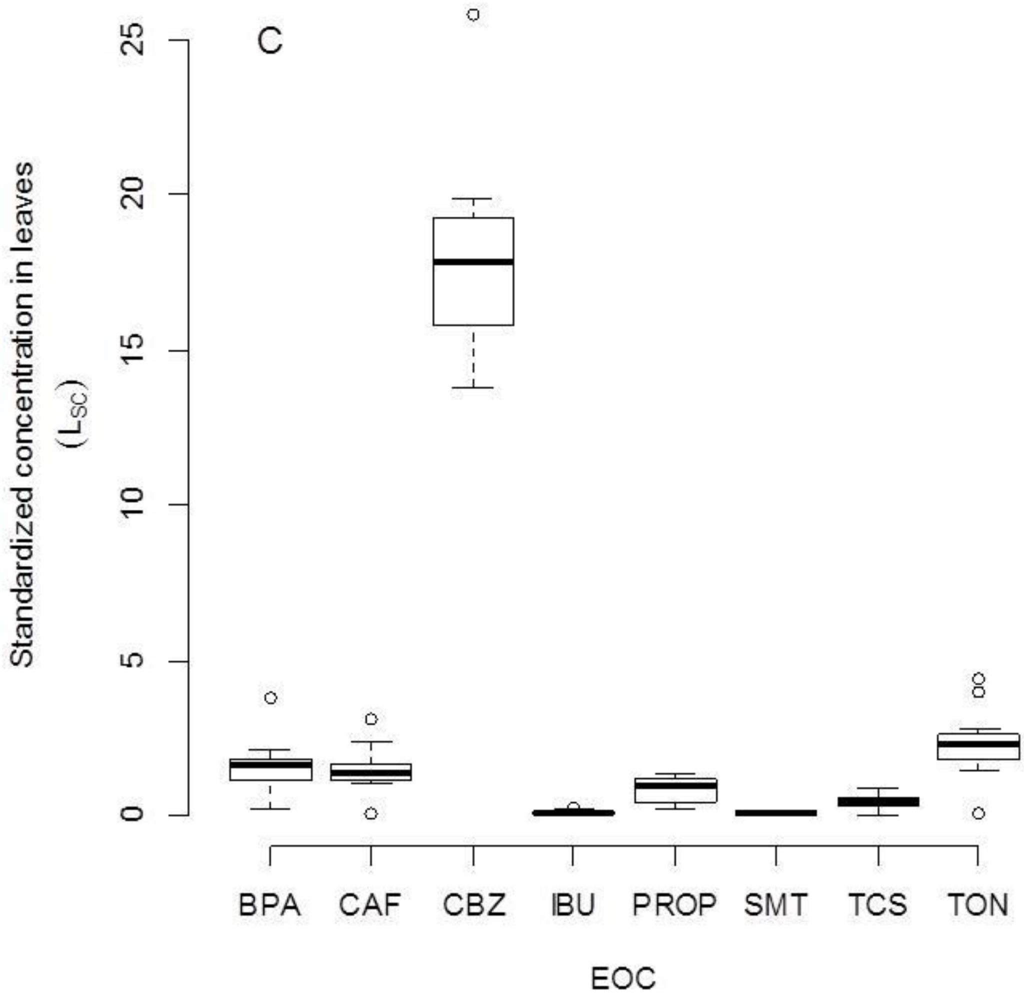

C
Standardized concentration in leaves (L_{SC})
0
5
10
15
20
25
BPA
CAF
CBZ
IBU
PROP
SMT
TCS
TON
EOC

Figure 1C.

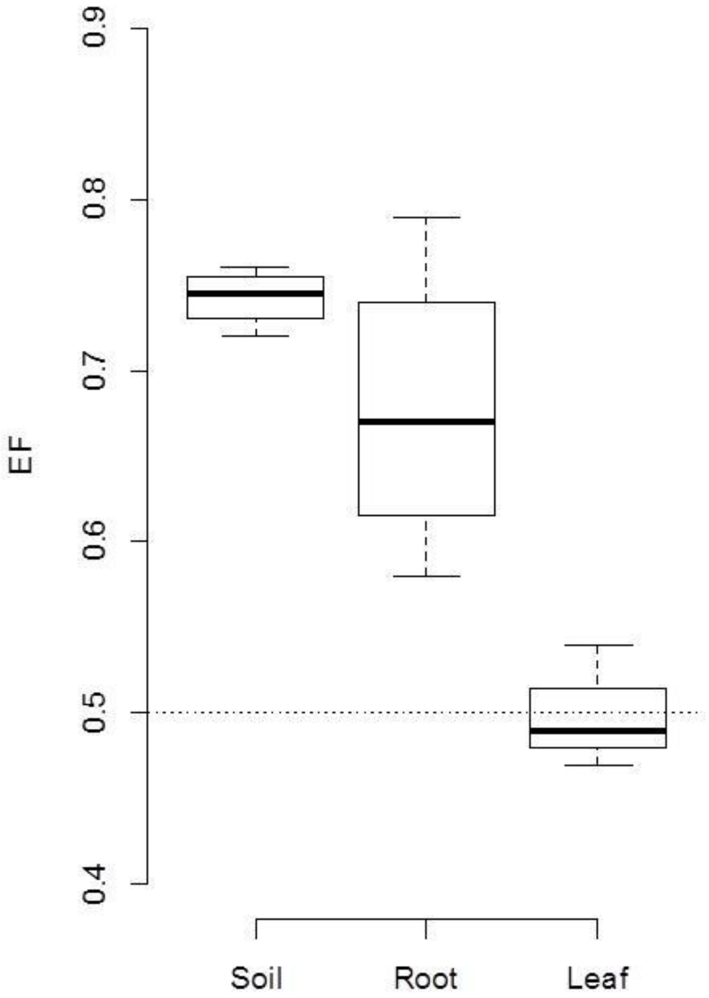


Figure 2.

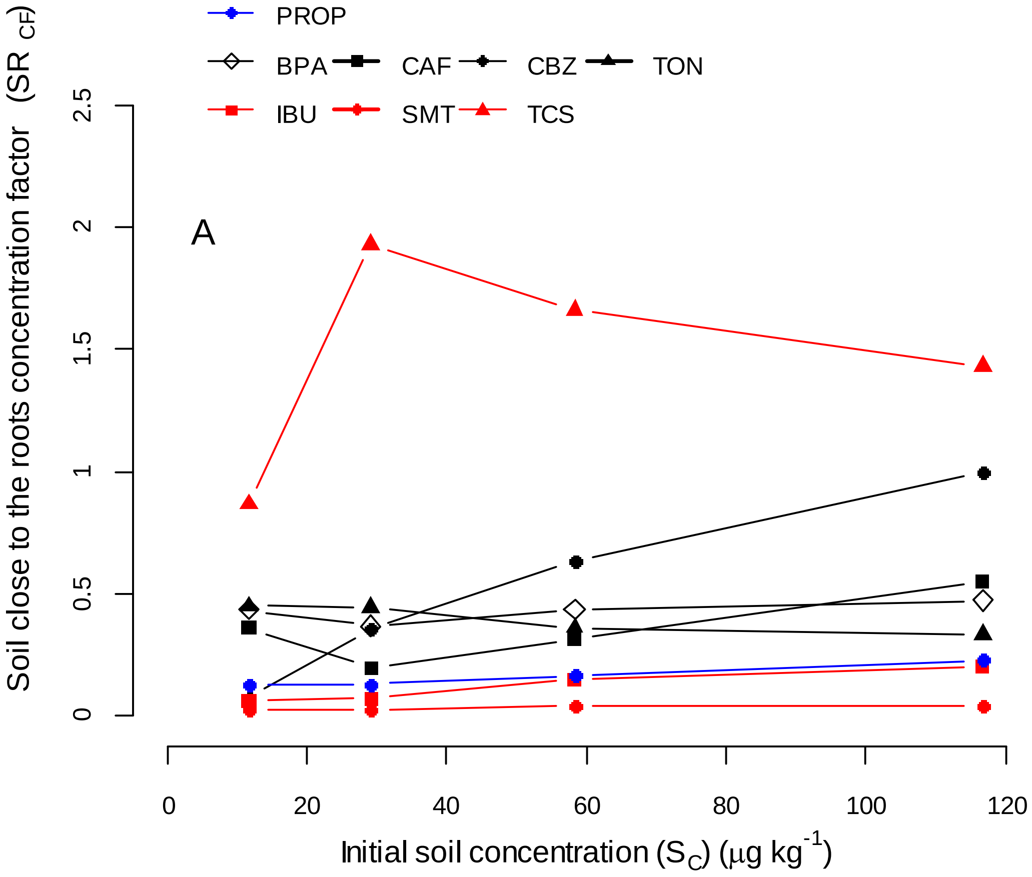

PROP
BPA
CAF
CBZ
TON
IBU
SMT
TCS
A
Soil close to the roots concentration factor (SR CF)
0
0.5
1
1.5
2
2.5
0
20
40
60
80
100
120
Initial soil concentration (S_C) (µg kg-1)

Figure 3A.

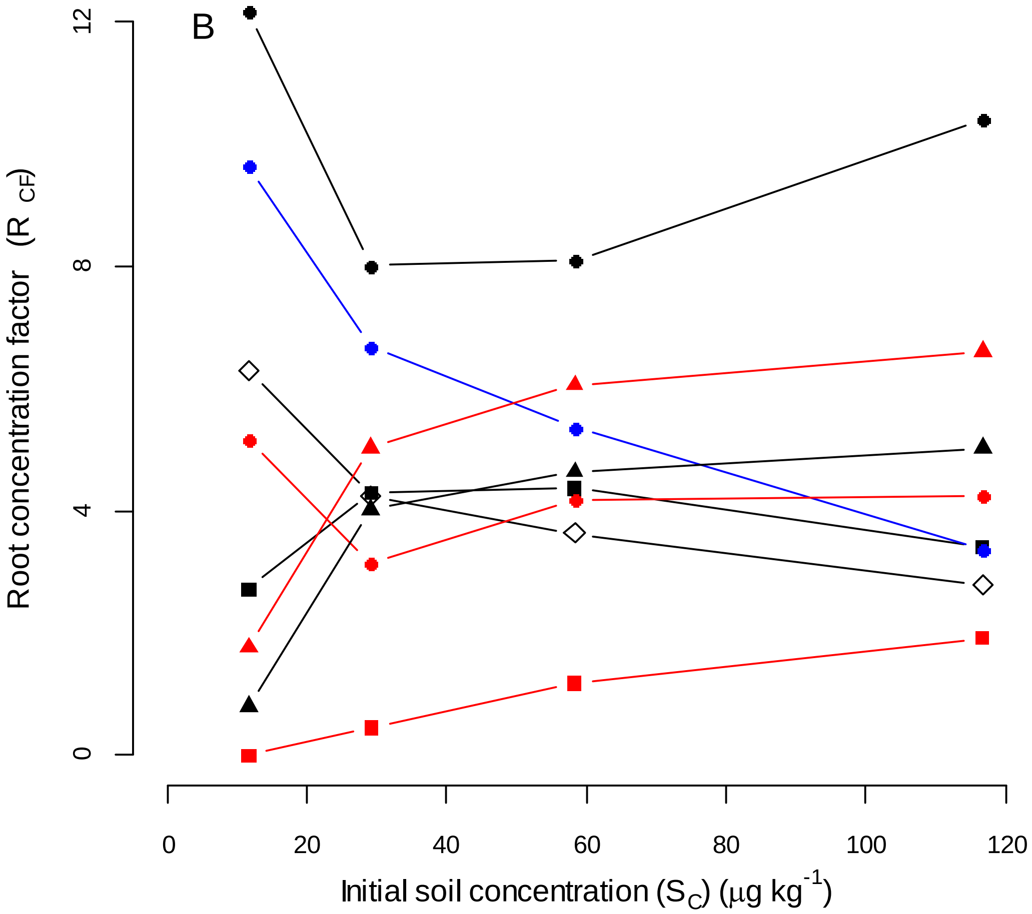

B
Root concentration factor (R CF)
0
4
8
12
0
20
40
60
80
100
120
Initial soil concentration (S_C) (µg kg^{-1})

Figure 3B.

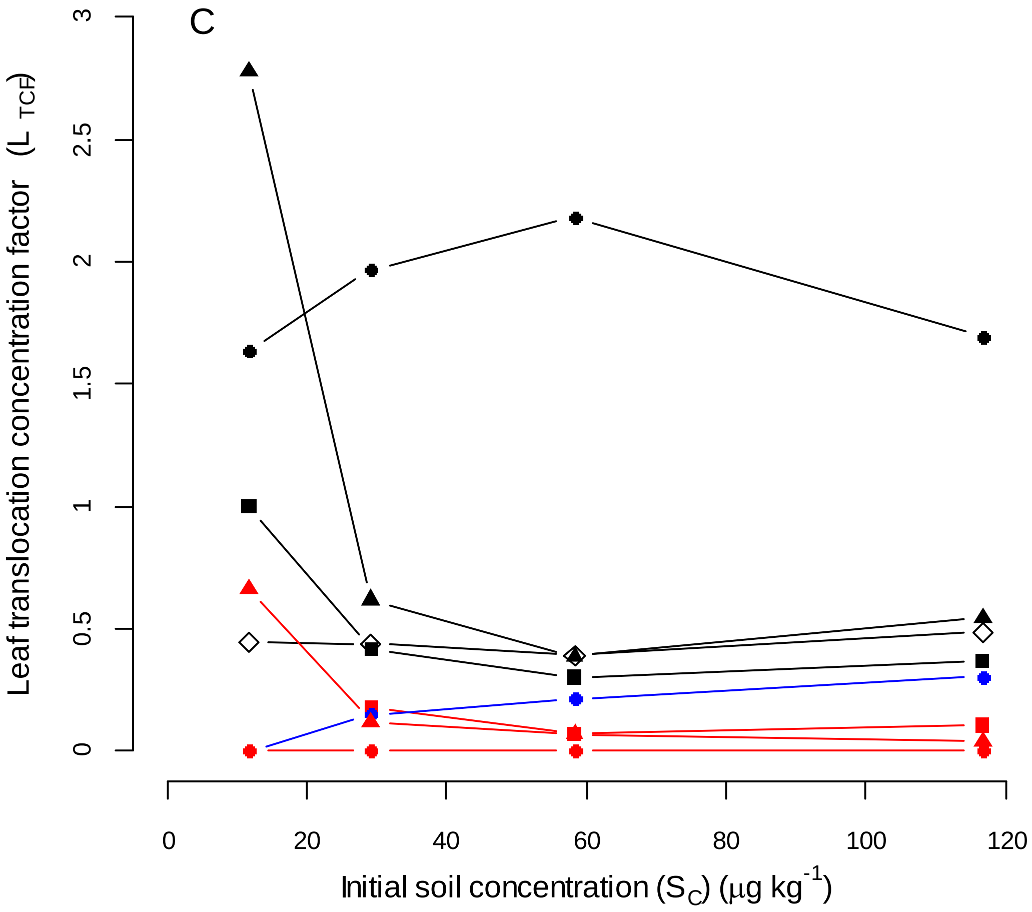

C
Leaf translocation concentration factor (L_{TCF})
0
0.5
1
1.5
2
2.5
3
0
20
40
60
80
100
120
Initial soil concentration (S_C) (µg kg^{-1})

Figure 3C.

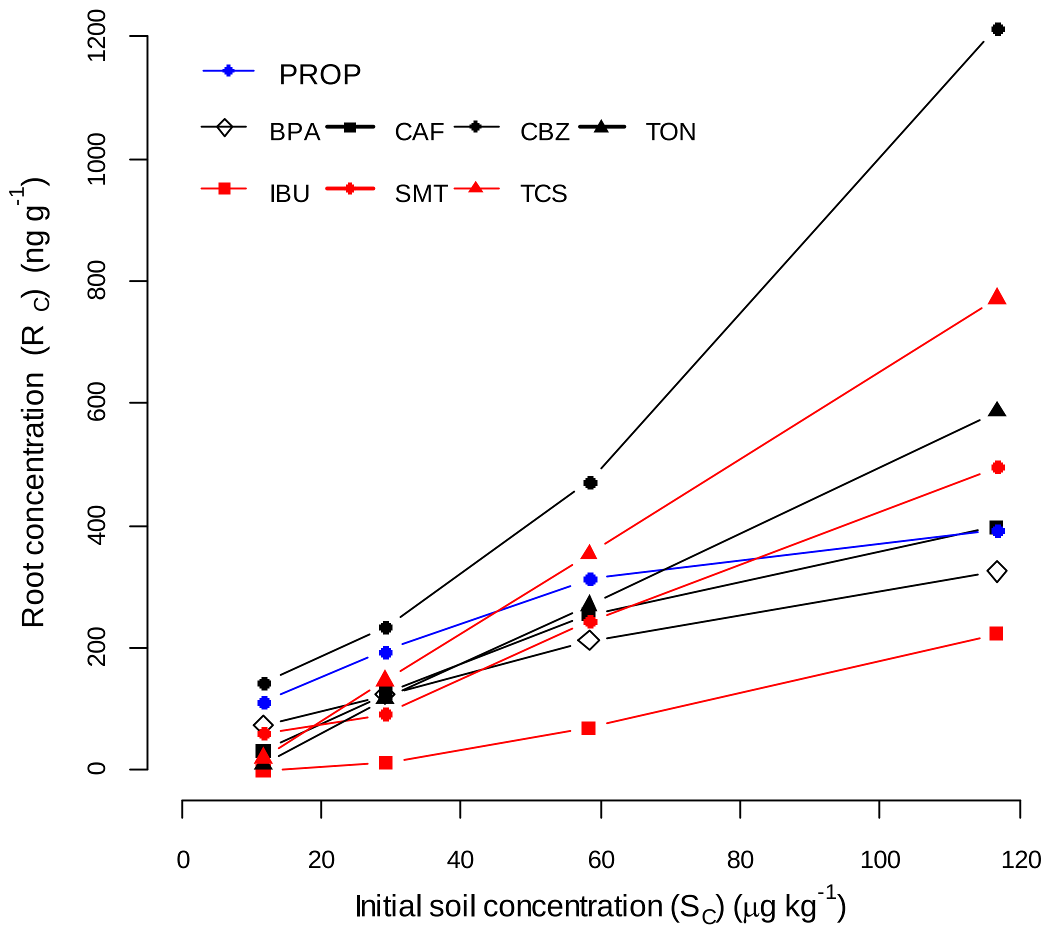

PROP
BPA
CAF
CBZ
TON
IBU
SMT
TCS
Root concentration (R C) (ng g-1)
0
200
400
600
800
1000
1200
0
20
40
60
80
100
120
Initial soil concentration (SC) (µg kg-1)

Figure 4.

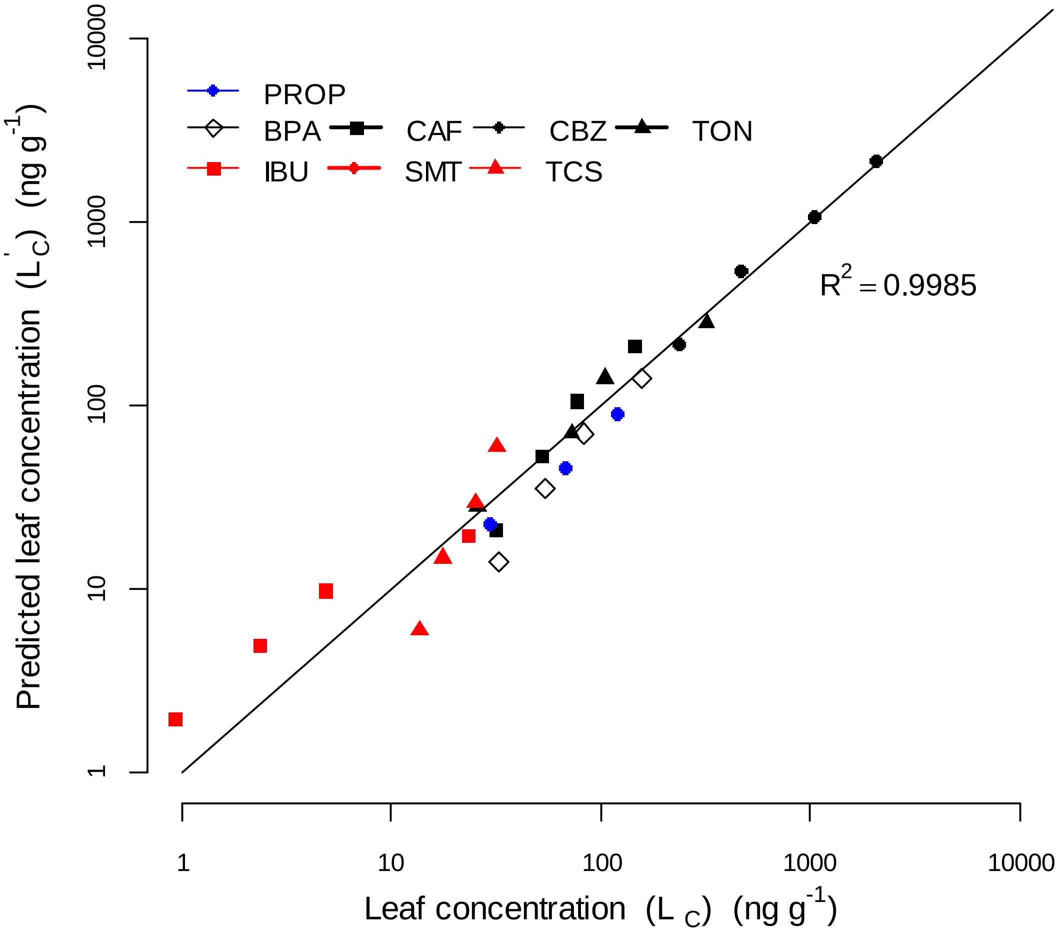

PROP
BPA
CAF
CBZ
TON
IBU
SMT
TCS
R² = 0.9985
Predicted leaf concentration (L'C) (ng g-1)
Leaf concentration (L C) (ng g-1)
1
10
100
1000
10000
1
10
100
1000
10000

Figure 5.

Supplementary Information for

Estimate of uptake and translocation of emerging organic contaminants from irrigation water concentration in lettuce grown under controlled conditions

Carles Hurtado[a], Carmen Domínguez[a], Lorea Pérez-Babace[a], Núria Cañameras[b], Jordi Comas[b], Josep M. Bayona, [a]*

[a]Environmental Chemistry Department, IDAEA–CSIC, Jordi Girona 18-26, E-08034 Barcelona, Spain

[b]Department of Agri-Food Engineering and Biotechnology DEAB-UPC, Esteve Terrades 8, Building 4, E-08860, Castelldefels, Spain

1.1 Materials and Reagents

Internal standard triphenylamine (TPhA, 98 %) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Trimethylsulfonium hydroxide (TMSH) was obtained from Fluka (Buchs, Switzerland). 10,11-Dihydrocarbamazepine (DHCBZ, 99 %), 2,2'-dinitrobiphenyl (DNBP, 97 %), 2-(2,4,5-trichlorophenoxy)propionic acid (FEN, Pestanal) and sulfamethoxazole (SMX, 99 %) were purchased from Sigma-Aldrich; tonalide-d3 (TON-D3) was purchased from Dr. Ehrenstorfer (Ausburg, Germany).

Florisil was purchased from Merck (Darmstadt, Germany). Sodium sulfate anhydrous and sodium chloride were purchased from Fluka (Buchs, Switzerland). Disodium hydrogen citrate sesquihydrate and trisodium citrate dihydrate were obtained from Sigma-Aldrich. Suprasolv® grade acetone, methanol, hexane, ethyl acetate and LiChrosolv® grade acetonitrile were purchased from Merck. Hydrochloric acid (37% v/v) and potassium carbonate (98 %) were purchased from Panreac (Barcelona, Spain). The Na_2SO_4 was baked for 5 hours at 450 ºC in a muffle furnace before using. Reagent water was deionized in the laboratory using the ultrapure water system Arium 611 from Sartorius (Aubagne, France).

(*R*)-(+)-α-methylbencylamine for chiral derivatization (*R*-1-PEA, ≥ 99%), triethylamine (TEA, ≥ 99%) and ethyl chloroformate (ECF, 97%) were purchased from Sigma-Aldrich. Strata-X, Polymeric HLB-Phase, solid phase extraction (SPE) cartridges (30 mg / 3 mL) were purchased from Phenomenex (Torrance, CA, USA).

1.2 GC-MS/MS determination

BPA, CAF, CBZ, IBU, TON and TCS were analyzed by GC-MS/MS. Methylation of the acidic carboxyl group for both vegetal tissue and soils extracts was performed in a programmed temperature vaporizing (PTV) injector of the gas chromatograph by adding 10 µL TMSH to a 50 µL sample aliquot before injection. A volume of 5 µL was injected into a Bruker 450-GC gas chromatograph coupled to a Bruker 320-MS triple quadrupole mass spectrometer (Bruker Daltonics, Billerica, MA, USA) fitted with a 20 m × 0.18 mm ID, 0.18 µm film thickness Sapiens X5-MS capillary column coated with 5 % diphenyl 95 % dimethyl polysiloxane from Teknokroma (Sant Cugat del Vallès, Spain). The PTV was set at 60 ºC for 0.5 min and rapidly heated to 300 ºC at 200 ºC min^{-1}, and hold for 7 min. Then the injector was cooled to initial 60 ºC at 200 ºC min^{-1}. The oven temperature was held at 60 ºC for 3.5 min and then the temperature was programmed at 30 ºC min^{-1} to a 150 ºC and finally at 8 ºC min^{-1} to 320 ºC, holding the final temperature for 6 minutes. Gas flow rate was set at 0.6 mL min^{-1}. Ion source temperature and the transfer line both were held at 250ºC. A solvent delay of 8 minutes was applied. Argon gas was used for CID at a pressure of 1.8 mTorr, and the optimum collision energy (CE) was selected for each transition.

Qualitative and quantitative analysis was performed based on retention time and selected reaction monitoring (SRM) mode of two product ions, and the ratio between the product ions (Table S1). The limit of detection (LOD) and the limit of quantitation (LOQ) for both vegetal tissue and soil were defined as the mean background noise in a blank triplicate plus three and ten times, respectively, the standard deviation of the background noise from three blanks. LODs and LOQs were compound dependent and for leaves and roots ranged from 0.8 to 5 ng g^{-1} dry weight (dw) and for soil ranged from 0.5 to 1 ng g^{-1} dw. The recoveries of the surrogates added can be seen in Table S4.

1.3 LC-MS/MS determination

Extract aliquots were evaporated to dryness and reconstituted with methanol:water (20:80, v/v) for SMT and PROP determination by LC-MS/MS. A TSQ Quantum triple-stage quadrupole mass spectrometer equipped with and ESI source (Thermo Fischer Scientific, San Jose, CA, USA), a Finnigan Surveyor MS Pump Plus and an HTC PAL autosampler (CTC Analytics, Zwingen, Switzerland) were used for LC-MS/MS determination.

The chromatographic separation was performed on a Kinetex® C18 Phenomenex® (50 × 2.1 mm, 2.6 µm). The mobile phase consist of water (A) and methanol (B) both solvents with 0.1 % formic acid and is set at 350 µL min^{-1}. The elution started at 20 % B for 1 min and was then linearly ramped up to 99 % B in 14 min, where it was held for 1 min before returning to the initial conditions in 1 min. The injection volume was 5 µL, and the column was maintained at 35 °C. The MS/MS determination was carried out in ESI positive ion mode with the spray voltage at 5.0 kV and the optimum tube lens voltage (TL) were optimized for each m/z. The ion transfer temperature was set at 250 °C. Nitrogen (purity, >99.999 %) was used as a sheath gas, ion sweep gas, and auxiliary gas at 70 psi. Data were acquired in the selected reaction monitoring (SRM) mode. Argon gas was used for CID at a pressure of 1.3 mTorr, and the optimum collision energy (CE) was selected for each transition (Table 2SI).

Qualitative and quantitative analysis was performed based on retention time and SRM mode of two product ions, and the ratio between the product ions as confirmation. The limit of detection (LOD) and the limit of quantitation (LOQ) for both vegetal tissue and soil were calculated as the mean background noise in a blank triplicate plus three and ten times, respectively, the standard deviation of the background noise from three blanks. LODs and LOQs were compound dependent and for leaves and roots ranged from 2.1 to 3.2 ng g^{-1} dry weight (dw) and for soil ranged from 0.05 to 0.10 ng g^{-1} dw respectively. Limits of detection (LODs) and limits of quantification for each compound in the different compartments are presented in Table S3.The recoveries of the spiked surrogates can be seen in Table S4.

1.4 Chiral derivatization of IBU

The derivatization procedure was described by Hashim and Khan[1]. The extracts were subjected to chiral derivatization by adding 30 µL of TEA (50mM in acetonitrile) and 40 µL of ECF (60mM in acetonitrile). This mixture was sonicated for 2 min and 10 µL of *R*-1-PEA (0.5 M in acetonitrile) were added. Then, the mixture was again sonicated for 2 min. Sulfuric acid 0.1 M and ultrapure water were added to stop the reaction, lower the pH and prepare the sample for further extraction of the diastereomeric derivatives.

The SPE cartridges were initially conditioned with 1.5 mL of ethyl acetate, 1.5 mL of methanol and 1.5 mL of ultra pure water adjusted to pH 9.5. The aqueous solutions were passed through the cartridges under gravity and the cartridges were rinsed twice with 1.5 mL of ultra pure water adjusted to pH 9.5. The cartridges were then dried under vacuum for 10 min. Finally, the amide derivatives were eluted with ethyl acetate (1 mL) to 2 mL GC vials.

The ibuprofen derivatives analysis was performed on a Trace GC-MS 2000 gas chromatograph – mass spectrometer (GC-MS) equipped with a 20 m × 0.18 mm ID, 0.14 µm film thickness TRB-50 column coated with (50%) diphenyl-(50%) dimethyl polysiloxane from Teknokroma. The carrier gas flow rate was 0.6 mL min^{-1}. 1 µL samples were injected in splitless mode and the injector temperature was set at 280 ºC. The oven temperature was held at 65 ºC for 2 min and then the temperature was programmed at 15 ºC min^{-1} to 120 ºC, at 6 ºC min^{-1} to 220 ºC and 12 ºC min^{-1} to 310 ºC, holding the final temperature for 10 min. Mass spectrometric ionization was undertaken in electron impact (EI) mode (70 eV) and the GC interface temperature was held at 270 ºC. Acquisition was performed in single-ion monitoring (SIM) mode with dwell times ranging from 0.300 to 0.190 s depending on the time segment, to achieve a minimum of 7 points per GC peak. The ions 161/119/105 (25 - 30 min) were monitored for ibuprofen derivatives and 245 (16 - 25 min) for internal standard tryphenylamine.

Table S1. Monitoring ions in GC-MS/MS

Segment	Compound	RT (min)	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)
1	IBU	11.02	161*	91	23
			220	161	11
2	FEN	13.68	196*	132	20
			284	198	15
3	CAF	14.79	194*	109	14
			194	55	20
3	TON	14.96	258*	243	10
			243	187	13
3	TON-d3	14.97	261*	246	10
			246	190	13
4	CBZ	16.81	193*	191	23
			193	167	18
4	DHCBZ	17.58	195*	152	30
			195	180	18
4	TPhA	17.16	245*	167	30
			245	141	21
5	BPA	17.74	241*	133	15
			241	211	17
5	DNBP	17.95	198*	168	15
			198	138	25
6	TCS	18.25	302*	252	19
			302	189	37

* Transition used for quantification

Table S2. Monitoring ions in LC-MS/MS (ESI)

Segment	Compound	RT (min)	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)
1	SMT	3.51	279*	149	17
			279	186	18
2	SMX	3.82	254*	183	17
			254	155	25
3	PROP	4.75	260*	156	16
			260	92	29

* Transition used for quantification

Table S3. Limits of detection (LOD) and quantification (LOQ) of the selected ECs in the three compartments studied

Compound	Compartment	LOD (ng g^{-1} dw)	LOQ (ng g^{-1} dw)
BPA	**Soil**	0.91	0.98
	Root	3.9	4.3
	Leaf	4.5	5.3
CAF	**Soil**	0.52	0.58
	Root	1.2	1.3
	Leaf	1.5	1.6
CBZ	**Soil**	0.49	0.54
	Root	1.1	1.2
	Leaf	1.3	1.5
IBU	**Soil**	0.47	0.51
	Root	1.1	1.2
	Leaf	0.80	0.89
PROP	**Soil**	0.81	0.93
	Root	2.3	2.9
	Leaf	5.3	6.0
SMT	**Soil**	0.49	0.54
	Root	0.77	0.86
	Leaf	3.9	4.3
TCS	**Soil**	0.41	0.44
	Root	0.85	0.91
	Leaf	0.93	1.2
TON	**Soil**	0.53	0.60
	Root	1.1	1.3
	Leaf	1.1	1.4

Table S4. Recoveries of the surrogates added in each compartment.

Compound	Compartment	Recovery (%)
DHCBZ	**Soil**	52 ± 5
	Root	77 ± 6
	Leaf	81 ± 7
DNBP	**Soil**	68 ± 5
	Root	65 ± 5
	Leaf	70 ± 8
FEN	**Soil**	41 ± 4
	Root	77 ± 6
	Leaf	71 ± 7
SMX	**Soil**	61 ± 12
	Root	38 ± 10
	Leaf	35 ± 7
TON-d3	**Soil**	59 ± 7
	Root	73 ± 12
	Leaf	68 ± 14

Table S5. Linear regression coefficients between the applied dose of EOC and the concentration found in each compartment.

Soil	Compound	Slope	R^2	p-value
	BPA	0.461	0.939	1.04E-10
	CAF	0.488	0.923	5.60E-10
	CBZ	0.894	0.899	4.63E-09
	IBU	0.188	0.937	1.30E-10
	PROP	0.211	0.710	1.32E-05
	SMT	0.040	0.879	1.70E-08
	TON	0.348	0.882	1.42E-08
	TCS	1.495	0.954	1.24E-11
Roots				
	BPA	3.030	0.926	4.21E-10
	CAF	3.625	0.931	2.54E-10
	CBZ	9.862	0.935	1.56E-10
	IBU	1.693	0.865	3.91E-08
	PROP	3.931	0.903	3.30E-09
	SMT	4.170	0.975	1.14E-12
	TON	4.891	0.958	1.59E-10
	TCS	6.396	0.931	2.60E-10
Leaves				
	BPA	1.394	0.917	1.05E-09
	CAF	1.296	0.968	7.30E-13
	CBZ	17.55	0.982	1.27E-14
	IBU	0.173	0.855	6.82E-08
	PROP	1.040	0.958	5.72E-12
	SMT	NA	NA	NA
	TON	2.533	0.911	1.73E-09
	TCS	0.320	0.910	1.90E-09

NA: not applicable

REFERENCE

1. Hashim, N. H.; Khan, S. J., Enantioselective analysis of ibuprofen, ketoprofen and naproxen in wastewater and environmental water samples. *J. Chromatogr. A* **2011,** *1218*, (29), 4746-4754.