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RESEARCH ARTICLE

Effects of applying biosolids to soils on the adsorption and bioavailability of 17α-ethinylestradiol and triclosan in wheat plants

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Abstract Biosolids contain inorganic and organic contaminants, including pharmaceutical and personal care products (PPCPs) that have accounted for a series of emerging contaminants, such as triclosan (TCS) and the hormone 17α-ethinylestradiol (EE2). The general aim of this study was to evaluate the effects of biosolid application on EE2 and TCS adsorption and bioavailability in soils through testing with wheat plants. For the bioavailability study, sand and two soils, Lampa and Lo Prado, were used. The sand and soils were treated using two biosolid application rates (0 and 90 mg ha^{-1}), and the EE2 and TCS concentrations in the biosolids were determined as 0.54 ± 0.06 and 8.31 ± 0.19 mg kg^{-1}, respectively. The concentration observed in wheat plants indicated that EE2 and TCS are mainly concentrated in the roots rather than in the shoots. Furthermore, the bioavailability of the compounds in plants depends on the properties of the contaminants and the soil. Adsorption studies showed that increasing the soil organic matter content increases the adsorption of TCS and EE2 on these substrates and that both compounds follow the Freundlich adsorption model. The desorption procedure indicated that availability for both TCS and EE2 depended on the soil type because TCS and EE2 were small in the Lampa soil with and without biosolid application and TCS increased by nearly 50% in the Lo Prado soil. The Lo Prado soil had an acidic pH (5.9) and the Lampa soil had a neutral pH of 7.3, and the organic carbon content was smaller.

Keywords Biosolids · Soil · Bioavailability · Adsorption · 17α-Ethinylestradiol · Triclosan

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Introduction

Compounds contained in pharmaceuticals and personal care products (PPCPs), such as 17α-ethinylestradiol (EE2) and triclosan (TSC), have been detected in biosolids and agricultural soils treated with biosolid amendments (Tamtam et al. 2008; Fick et al. 2009; McClellan and Halden 2010; Wu et al. 2009a, b). The removal of these compounds during wastewater treatment is not complete, allowing them to reach the ground environment following the application of biosolids to soils (McClellan and Halden 2010; Lozano et al. 2013). The uptake of these contaminants by plants grown in biosolid-treated agricultural soils has become an increasing source of interest because several studies have shown that plants can accumulate these compounds and that plant uptake is probably affected by the physicochemical properties of these contaminants and their interactions with the soil (Wu et al. 2012). Other studies have demonstrated that compounds such as EE2 and TCS can be specifically adsorbed to soils with higher organic matter contents (Karnjanapiboonwong et al. 2010a).

Several studies have assessed the endocrine disrupting potential of EE2 in water invertebrates (Goto and Hiromi 2003; Gross et al. 2001; Watts et al. 2002; Segner et al. 2003). EE2 can cause relevant biological effects at extremely low concentrations, affecting the hormone system of aquatic animals. Less than 1 ng/L EE2 is needed to cause male feminization (Purdom et al. 1994; Andrew et al. 2008). In addition, this

compound could reduce the reproductivity of animals steadily exposed to concentrations as low as parts per trillion (Länge et al. 2001; Kidd et al. 2007; Xu et al. 2008). Because EE2 is a hydrophobic compound and has an octanol/water partition coefficient (log K_{ow}) of 3.67 (Bradley and Smith 2011), it has the tendency to sorb to organic matrices. Its low water solubility (4.8 mg/L) and low vapor pressure, combined with its hydrophobic character, indicate that the affinity of EE2 for the solid phase is likely to be relatively high (Langston et al. 2005); therefore, it is not eliminated completely in wastewater treatment plants and remains in the resulting sludge. When biosolids are used as fertilizers, the crops are exposed to synthetic estrogen, which can be taken up by plants and could cause phytotoxicity problems (Lai et al. 2002). Other studies have shown that estrogens are readily adsorbed on soils and sediments, which potentially limits their mobility and transport from soils to aquatic ecosystems where they may cause more damage (Hildebrand et al. 2006).

TCS is an antimicrobial agent that is widely used in personal care products. Because of its ability to inhibit antimicrobial growth, TCS is present in plastics, polymers, and textile products (De Vere and Purchase 2007; Orhan et al. 2007), as well as household products such as cutting boards and toys (Lozano et al. 2010). The main access route of TCS to the environment is through urban sewage wastewater because TCS is a hydrophobic compound with low volatility and is not totally removed at wastewater treatment plants; thus, TCS remains in the sewage sludge and is transported to biosolid-amended soils. Its popular use has resulted in the detection of TCS in environmental residues at concentrations of milligrams per kilogram, which suggests significant environmental contamination and bioaccumulation (Chalew and Halden 2009; Lozano et al. 2010). Several studies have demonstrated that TCS can cause resistance to antibiotics (Waller and Kookana 2009; Butler et al. 2012) and may accumulate in the tissues of organisms (Coogan and La Point 2008). It has been demonstrated that TCS can be taken up by plants and may cause phytotoxicity (Karnjanapiboonwong et al. 2011). Karnjanapiboonwong et al. (2010a, b) determined that triclosan in bean plants (*Phaseolus vulgaris)* is mainly found in plant roots rather than in plant shoots. The bioaccumulation of TCS has also been assessed in algae, with concentrations observed in the range of parts per billion and exceeding the values observed in the effluent waters of the treatment plant, which suggests TCS buildup (Coogan et al. 2007). Other authors examined triclosan phytoaccumulation in biosolid-amended soils using cabbage, zucchini, and grass and demonstrated that these plants can reduce TCS leaching at the phreatic level, resulting in decreased TCS persistence in agricultural soils (Aryal and Reinhold 2011). Other studies have assessed the fate of TCS in agricultural soils after biosolid application and observed steady decreases in the TCS content (Lozano et al. 2010; Jachero et al. 2015), which could be accounted for by biological breakdown (Liu et al. 2009). The application of biosolid amendments increases triclosan adsorption, potentially due to the addition of organic matter to soils (Wu et al. 2009a, b). Triclosan is an endocrine disruptor in aquatic species (Matsumura et al. 2005). A study with rats demonstrated hypothermia and a depressive effect on the central nervous system (Bedoux et al. 2012). Other studies have demonstrated that TCS can cause oxidizing stress in rats (Tamura et al. 2012) and exert adverse reactions on the immune system in humans and animals (Kawanai 2011). Honkisz et al. (2012) showed that 50 and 100 mM doses of triclosan resulted in a strong cytotoxic effect, which potentially affected placental growth and fetal growth in humans.

Bioavailability is a measure of the potential of a chemical compound to enter a biological receptor and is specific to the receptor, entry route, time of exposure, and matrix containing the contaminant (Semple et al. 2004). Bioavailability is controlled by several physicochemical processes, such as sorption/desorption, diffusion, and dissolution. One of the causes that could reduce the bioavailability could be by the low mass transference of the contaminant towards living organisms due to contaminant degradation (Cuypers et al. 2002). Assessing the bioavailability of hydrophobic organic contaminants in soils may be conducted by directly exposing various organisms to the sample for a given period before measuring the contaminant contents again (Semple et al. 2003).

The purpose of this study was to assess the effects of biosolid application to soils relative to EE2 and TCS adsorption and to determine the bioavailable concentrations of both compounds using wheat plants.

Material and methods

Reagents

Triclosan (97%) was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), and 17α-ethinylestradiol (99%) was obtained from Sigma-Aldrich (Milwaukee, WI, USA). Carbon 13-labeled TCS ($^{13}C_{12}$-TCS) was purchased at Wellington Laboratories (Ontario, Canada), and (20,21)-$^{13}C_2$-17α-ethinylestradiol was purchased from Cambridge Isotope Laboratories, Inc. (USA) for use as a surrogate standard. Hexachlorobenzene (HCB, 99.5% purity) was used as an internal standard and was purchased at Dr. Ehrenstorfer GmbH (Augsburg, Germany). *N*-Methyl-*N*-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) and the pyridine derivatizing agent were obtained from Sigma-Aldrich (Milwaukee, WI, USA). HPLC-grade ethyl acetate, methanol, acetone, hexane, and dichloromethane solvents were purchased from Merck (Darmstadt, Germany). Oasis HLB cartridges for solid phase extraction were obtained from the Waters Corporation (Milford, MA, USA). Nitrogen

and helium were purchased at Linde (Santiago, Chile) and were used in the final extract evaporation step and as the chromatographic carrier gas, respectively.

Soil and biosolid samples

Two soil samples, Lampa and Lo Prado, were obtained from the Santiago Metropolitan Region in Chile. The soil samples were collected from the soil surface (0–20 cm), and compound samples obtained at each sample site were air dried and passed through a 2-mm sieve. Biosolids from anaerobic digestion were collected at a wastewater treatment plant in the Santiago Metropolitan Region and were air-dried and passed through a 2-mm sieve.

The pH and organic carbon content were determined. Texture analysis was only performed on soil samples (Sadzawka et al. 2006).

Spiking the biosolid with EE2 and TCS

The biosolids were spiked with 10 mg kg^{-1} of EE2 or TCS using the following procedure: 500 g of biosolids was placed in a separate 500-mL round-bottom flask, and 10 mg kg^{-1} in acetone of either EE2 or TSC was added. The biosolid sample was covered with acetone and evaporated in a rotary evaporator at 200 rpm for 24 h at room temperature in the dark to prevent photodegradation. Next, the biosolid was transferred to a dish and left to dry in the dark. The EE2- or TCS-spiked biosolids were later added to pots with 500 g soil at a rate of 90 mg ha^{-1}. Soils or sand and biosolid were mixed until homogeneous before seeding.

Determination of total EE2 and TCS concentrations in the soils and biosolids

The samples (0.5 g) of soil, sand, biosolid, soil-biosolid, sand-biosolid, and soil with biosolid spiked with EE2 or TCS were spiked with the surrogate standard (20,21)-$^{13}C_2$-17α-ethinylestradiol or $^{13}C_{12}$-TCS (200 ng g^{-1}) and extracted three times using ethyl acetate (3 × 5 mL) in a sonication bath (15 min each step). Then, the samples were centrifuged for 15 min at 2500 rpm (Ying and Kookana 2005) and the extracts were concentrated to dryness under a gentle nitrogen stream before dissolving in 5 mL methanol. To each extract sample, 5 mL Milli-Q water was added. Extract purification was carried out using Oasis HLB solid phase extraction cartridges. The cartridges were successively conditioned using 3 mL of each of the following solvents: methanol, acetone, dichloromethane (DCM), and hexane (Shaogang and Chris 2007). The samples were loaded into the cartridges and washed three times with 2 mL hexane and twice with 3 mL Milli-Q water. The compounds were eluted three times in a 3 mL 50:50 (*v*/*v*) methanol/acetone mixture. The eluate was evaporated under nitrogen and reconstituted in 1 mL ethyl acetate for GC-MS analysis.

GC-MS

Before GC-MS analysis, the samples were derivatized. First, 100 μL of the eluate was transferred to an amber glass vial and evaporated with nitrogen gas. Next, 50 μL *N*-methyl-*N*-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) and 50 μL pyridine were added to the dry eluate and heated to 80 °C for 30 min. After derivatization was complete, the mixture was cooled to room temperature. The derivatized extracts were injected (2 μL) into a gas chromatograph (Thermo Fisher, Focus model) with a mass spectrometry detector, an ISQ and an SSL injector. The electron impact (EI) ionization mode was used with 99.9999% pure helium as a carrier gas at a flow rate of 1 mL min^{-1}. A Restek Rtx-5 MS capillary column with the following dimensions was used with a maximum temperature of 350 °C: 30 m long, 0.32 nm ID, 0.25 μm df film thinness. The initial oven temperature was 100 °C, which was maintained for 1 min before heating to 300 °C with a rate of increase of 10 °C/min. The chromatographic run required 21 min with a solvent delay of 7 min, a transfer line at 250 °C, an ionization source at 200 °C, a carrier gas flow rate of 1 mL/min, and an injector temperature of 240 °C in the splitless mode. The ions used to quantify and confirm TCS were *m*/*z* 345 and 347, the ions used to quantify and confirm $^{13}C_{12}$-TCS were *m*/*z* 357 and 359, the ions used to quantify and confirm EE2 were *m*/*z* 425 and 440, and the ions used to quantify and confirm (20,21)-$^{13}C_2$EE2 were *m*/*z* 427 and 442. The same extraction methodology, purification, and GC-MS analysis were used to determine the TCS concentrations in the soil, sand, plants, and biosolids.

Determination of the bioavailable EE2 or TCS fraction

Plastic pots (12.5 cm diameter and 11 cm high) were used for the plant assays. The pots were fitted at the bottom with plastic grids to support added quartz to prevent sample loss. The pots were filled with the different soil, sand, and soil-biosolid samples, and biosolids were added at 0 and 90 mg ha^{-1} rates. Three replicates of each treatment were included. Natural biosolids and biosolids spiked with EE2 or TCS were used separately for the mixtures.

The rates of biosolid addition were based on Chilean regulations, which allowed biosolid application at 90 Mg ha^{-1} in degraded soils. Pots containing an equivalent of 500 g dry weight of soil were irrigated to field capacity and allowed to stand for 15 days before sowing with wheat. Next, 10 g of wheat seed was planted in each pot. After the germination period (approximately 1 week), the automatic greenhouse lighting was set to produce a 14/10 h (day/night) cycle with a temperature of 25 °C ± 5 °C. The moisture content was

controlled by watering daily with distilled water at 60–70% of the soil field capacity. After the growth period (30 days), the wheat seedlings were removed from each pot and washed with distilled water. The roots and shoots from each pot were separated and oven-dried at 30 °C. For analysis, 0.5 g of sample was placed in a conical glass tube. Then, 5 mL HPLC-grade ethyl acetate was added and enriched with the standard surrogate corresponding to each compound, $^{13}C_{12}$-TCS or (20,21)-$^{13}C_2$-17α-ethinylestradiol, at a concentration of 200 ng g^{-1}. The sample was sonicated, and the extracts were purified using an Oasis HLB cartridge according to the technique described above. Also, controls and the respective blank were run. Next, the eluate was analyzed by GC-MS.

Determination of the bioaccumulation factor of EE2 and TCS

The bioaccumulation factor was calculated considering the compound concentration in the plant relative mass and its concentration in the soil on a dry mass basis.

$$\mathrm{BCF} = \frac{\text{Concentration in plant } \left(\mu g / g\right)}{\text{Concentration in soil } \left(\mu g / g\right)}$$

EE2 and TCS adsorption experiments

Adsorption experiments were conducted in batch. Working solutions of each compound were prepared over a range of 0.1–4.0 mg L^{-1} in 0.01 M $CaCl_2$. Soil and soil-biosolid mixtures were placed in glass tubes using a 1:30 sample/solution ratio in duplicate. In addition, a control sample of each solution was included to ensure no compound adsorption on the tube or loss by volatilization. The solutions were placed in an orbital shaker at 150 rpm for 24 h then centrifuged for 15 min. Finally, the supernatants were collected and analyzed using a liquid chromatography with diode array detector (HPLC-DAD) on a Waters HPLC instrument set provided with binary pump (Waters 1525) Atlantis column dC18 (5 μm; 250 mm × 4.6 mm), a UV/visible detector with diode array (Waters 2998), and a Rheodyne manual injector valve, model 7725i with 20 μL sample loop. The results of the adsorption studies were interpreted using the Freundlich model or a linear mathematical model to obtain the adsorption isotherms.

To determine compound desorption, only some of the points of the adsorption study were used, corresponding to concentrations of 0.5, 1.5, and 3.5 mg L^{-1} EE2 or TCS in duplicate. To each glass tube, 5 mL of 0.01 M $CaCl_2$ was added. The suspensions were equilibrated for 24 h using an orbital shaker at 150 rpm before centrifuging for 15 min. Finally, supernatants were collected and desorbed TCS or EE2 was determined using HPLC-DAD.

Statistical analysis

Linear correlation tests were applied to assess the relationship between the plant EE2 or TCS concentration and the estimated bioavailable EE2 or TCS fraction obtained from cyclodextrin extraction. All statistical tests were carried out using Statgraphic 5.0 software. The level of significance for all comparisons was 95% ($p < 0.05$). ANOVA was used to evaluate the differences between treatments.

Results and discussion

Physical and chemical sample characterization

Table 1 shows some general characteristics of the soil and biosolid samples. The Lo Prado soil had an acidic pH (5.9), and the Lampa soil had a neutral pH of 7.3 and an organic carbon content that was smaller than that of the Lo Prado soil. As expected, the biosolid had greater organic carbon content and a pH value of 6.8. In addition, the Lampa and Lo Prado soils had loam and sandy loam textures, respectively.

Both soils showed no presence of 17α-ethinylestradiol or triclosan. Instead, the biosolids contained 0.54 ± 0.06 and 8.31 ± 0.19 mg kg^{-1} EE2 and TCS, respectively.

Determination of the bioavailable fraction of EE2 and TCS in wheat plant growth in sand and soils treated with and without biosolids

The concentrations of EE2 and TCS in wheat plants showed that both compounds for all treatment were mainly found in the wheat roots; however, this difference was greater for TCS than for EE2. The abilities of different plant species to uptake organic compounds could vary widely, with the lipid content being responsible for affecting the uptake of hydrophobic organic contaminants through roots (Wu et al. 2012). Other researchers have observed that roots have a high potential for building up hydrophilic organic contaminants (Karnjanapiboonwong et al. 2011). Figure 1 shows that the two compounds under study are mainly taken up by wheat

Table 1 Some physical and chemical properties of soils and biosolids

	Lampa	Lo Prado	Biosolid
pH	7.3	5.9	6.8
Organic C (%)	1.1	2.5	20.6
Organic matter (%)	1.8	4.4	
Sand (%)	57	78	–
Clay (%)	20	8.0	–
Silt (%)	23	14	–
Texture	Loam	Loamy sand	–

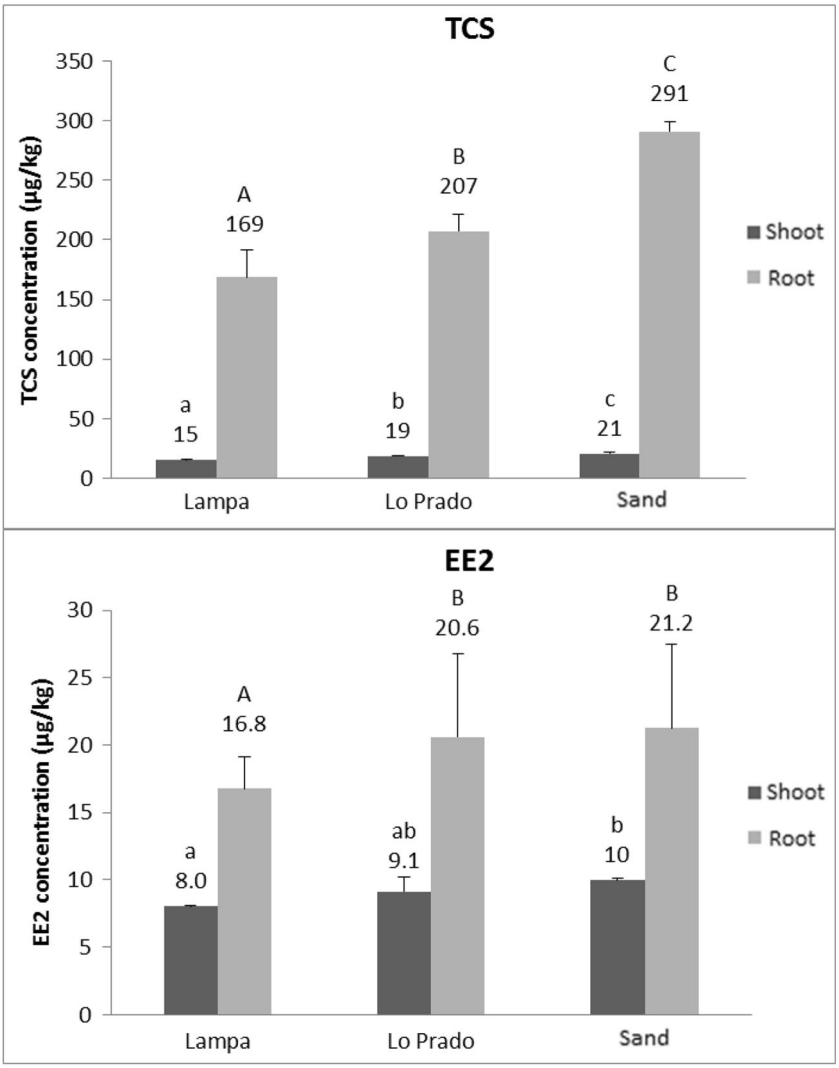

Fig. 1 TCS and EE2 concentration in the shoots and roots of plants grown in sand and Lampa and Lo Prado soils, treated with 90 mg ha^{-1} rate biosolid. *Error bars* are given as standard deviation ($n = 3$)

plants grown in biosolid-treated sand, especially TCS. This result may be due to the absence of organic carbon in sand compared with the amounts found in the Lampa and Lo Prado soils of 1.1 and 2.5%, respectively, because some researchers have determined that lower soil organic carbon contents correspond with greater TCS bioavailability (Karnjanapiboonwong et al. 2010b; Jachero et al. 2015). As shown in Fig. 1, the concentrations of both EE2 and TCS found in the plants grown in the Lo Prado soil were higher than those found in the plants grown in the Lampa soil. This result could be related to the pH value of the soils and the pKa value of the compounds because at two pH units below the pKa of the compounds molecules are neutral. In this case, the pH of the Lo Prado soil is 5.9 and the pKa of the compounds is 7.9 and 10.12 for TCS and EE2, respectively; thus, both compounds are found in their neutral form, which favors the transport of compounds to the roots. Molecular dissociation reduces bioaccumulation in plant roots because ions cross biomembranes at a slower rate than neutral molecules. Both TCS and EE2 are weak acids that form anions when they dissociate and are not easily taken up by plants, because plant cells in the cell membrane have a negative electric potential that exerts a repulsive force on the negatively charged anion (Wu et al. 2013). However, because both compounds are found in their neutral form, they are readily taken up by plants and their bioaccumulation increases with decreasing dissociation, which is the case for TCS and EE2 in the Lo Prado soil. As shown in Fig. 1, the TCS concentration in roots is much higher than that in shoots, and the EE2 concentration present in roots is only twice that found in shoots. In addition, the TCS concentration in the roots and shoots is higher than the EE2 concentration; however, it must be taken into account that the amount of TCS in the biosolids is greater than that of EE2.

Figure 2 shows the results obtained when performing the same experiment described above but using biosolids spiked separately with 10,000 µg kg^{-1} TCS and EE2. A higher concentration in the roots than in the shoots may be observed for both compounds. The TCS concentrations in wheat plants grown in sand were greater than the concentrations in wheat plants grown in the Lo Prado soil, which were both higher than the

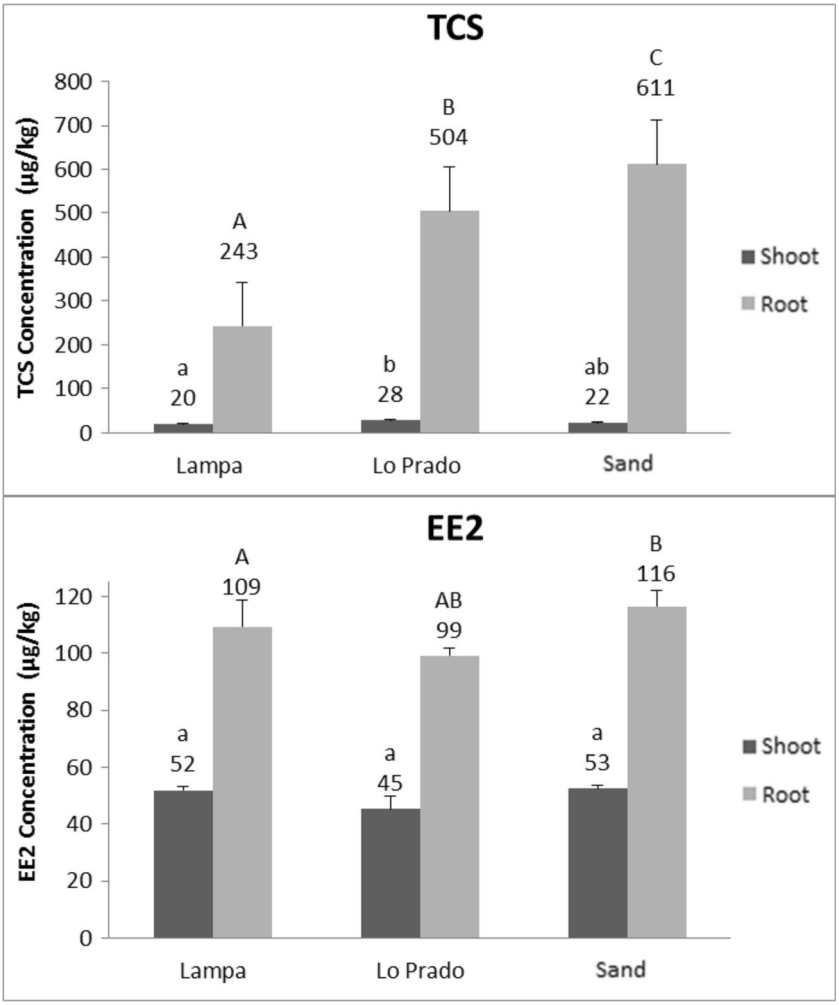

Fig. 2 Concentration of TCS and EE2 in the shoots and roots of plants grown in sand and Lampa and Lo Prado soils, treated with rate of 90 mg ha^{-1} of biosolid spiked with 10 mg kg^{-1} of TCS or EE2. *Error bars* are given as standard deviation ($n = 3$)

concentrations found in the plants grown in Lampa soil. This result was also observed for the wheat plants grown in sand and in soils treated with natural biosolids (Fig. 1). Regarding EE2, the concentrations found in the plants grown in sand were higher than those in the plants grown in the Lo Prado and Lampa soils. However, unlike the results in plants grown in soils treated with natural biosolids, the EE2 concentration was lower in the plants grown in the Lo Prado soil than in the Lampa soil, although this difference was not statistically significant ($p > 0.05$) compared with the case of TCS ($p < 0.05$).

As shown for the assay with natural biosolids, the TCS concentrations in the roots were higher than those in the shoots, and the EE2 concentrations in the roots were nearly twice those in the shoots. In addition, the TCS concentrations in the entire plant were higher than those of EE2 which reflects the initial biosolid concentration.

Wheat plant biomass

Wheat plant biomass was assessed to show the effects of the presence of EE2 and TCS in soils after biosolid application. Table 2 shows the biomass of the wheat plants obtained in soils and sand with and without biosolid application and in soils and sand with the application of biosolids spiked with

Table 2 Biomass of wheat plants grown in sand and soils with and without application of natural and spiked biosolids

Biosolid rates (mg ha^{-1})	Biomass (g)		
	Lampa soil	Lo Prado soil	Sand
Natural biosolid			
0	4.52 ± 0.63a	5.80 ± 0.57b	4.79 ± 0.45e
90	4.36 ± 0.78a	4.77 ± 0.22c	4.79 ± 0.33e
TCS-spiked biosolid			
90	4.52 ± 0.10 a	4.93 ± 0.34c	5.50 ± 0.33f
EE2-spiked biosolid			
90	4.18 ± 0.46a	3.82 ± 0.32d	5.10 ± 0.35ef

$n = 3$

For each soil and sand, values followed by same lowercase letter in each column show no significant differences for $p \geq 0.05$ according to Tukey HSD test

EE2 and TCS. A mass comparison was carried out using analysis of variance (ANOVA) to determine the existence of statistically significant differences in the resulting masses. The least significant difference test (LSD) was applied to the means with a confidence level of 5% ($p \geq 0.05$).

For plants grown in the Lampa soil, no significant differences ($p > 0.05$) were obtained in the wheat plant masses when they were grown in soils with and without the application of natural and spiked biosolids (both TCS and EE2); thus, no negative effects of these contaminants are observed for plants grown in this soil. In the case of the Lo Prado soil, no significant differences were obtained when wheat plants were grown in soils with the application of natural and TCS-spiked biosolids. However, differences were observed when the plants were grown in the soil without biosolid application. In this case, greater biomass was obtained relative to all of the other cases. Furthermore, when wheat was grown in the Lo Prado soil with EE2-spiked biosolids, the resulting biomass was significantly smaller than that obtained in the other cases. This result shows a negative effect of EE2 for plant growth in this soil.

The plants grown in sand showed no significant biomass differences in the cases with and without biosolids, both natural and TCS or EE2-spiked, but it did not show significant differences when grown in sand with the application of TCS-spiked biosolids, and without the application of natural biosolid, a greater biomass was obtained in the former case. As previously observed for the Lampa soil, no negative effect of compounds was observed in the plants. When assessing the effects of spiked biosolids on soils, it may be observed that the presence of EE2 hormones negatively affects plant growth, because EE2 hormones decreased the biomass as the amount of EE2 in the soil increased. For the Lampa soil, no negative effects of TCS on plant growth were observed because no significant differences were observed in any of the assessed cases. However, in the Lo Prado soil, the biomass values decreased in both cases of biosolid application.

A comparison of the biomass obtained in both soils allowed to observe that this difference in biomass was greater for plants grown in the Lo Prado soil in all cases, except for the plants grown in the EE2-spiked soil. This result coincided with the highest values of BCF found in Lo Prado soil. The generation of more biomass in this soil may be explained by its larger soil organic carbon content compared with the Lampa soil. The decrease in biomass in EE2-spiked soils was only important in the case of the Lo Prado soil. Thus, the presence of hormones would cause a negative effect on plant growth, which would depend on soil type. The lower biomass in soils with respect to sand could be explained by a combined effect of the soil type and phytotoxicity caused by the presence of these compounds, which in our case was more noticeable in the case of EE2 than TCS. Other researchers such as Liu et al. (2009) have found that TCS affects the growth of some plants; on the contrary, other researchers did not observe any effect with the presence of both compounds in the growth of pinto bean (Karnjanapiboonwong et al. 2011).

Determination of EE2 and TCS bioaccumulation factors using wheat plants grown in control soils and soils treated with biosolid

The bioaccumulation factor (BCF) describes the translocation of contaminants from soils to plants and is calculated using the equation relating the contaminant concentration found in the plant tissue to the concentration found in the soil (Karnjanapiboonwong et al. 2011). Table 3 shows the bioaccumulation factors calculated from the EE2 and TCS concentrations found in plants and in the different substrates used for plant growth. The greatest bioaccumulation factors of TCS and EE2 in the plant roots and shoots were found when sand was used as the substrate, followed by the Lo Prado and Lampa soils. The Lo Prado soil has higher organic matter than both sand and Lampa soil; this soil should have a higher adsorption capacity and therefore less bioavailability. It has been found that the bioavailability of pharmaceutical and personal care products in terrestrial environments is largely controlled by sorption processes (Karnjanapiboonwong et al. 2010a, b), and the adsorption isotherms obtained in both soils showed that the adsorption of both compounds was smaller in the Lo

Table 3 Bioconcentration factor (BCF) of TCS and EE2 in wheat plants grown in sand and in Lampa and Lo Prado soils, treated with natural biosolids and spiked biosolids at 90 mg ha^{-1} rates

TCS (μg kg^{-1})					
	Soil or sand	Shoot	Root	BCF shoot	BCF root
		Natural biosolid			
Lampa	367	15	169	0.041a	0.460a
Lo Prado	353	19	207	0.054b	0.586b
Sand	313	21	290	0.067c	0.927c
		Spiked biosolid			
Lampa	809	20	243	0.025a	0.300a
Lo Prado	777	28	504	0.036b	0.649b
Sand	689	22	611	0.032b	0.887c
		EE2 (μg kg^{-1})			
		Natural biosolid			
Lampa	54	8.0	16	0.148a	0.296a
Lo Prado	53	9.0	19	0.170b	0.358b
Arena	52	10	21	0.192c	0.404c
		Spiked biosolids			
Lampa	466	52	109	0.112a	0.233a
Lo Prado	432	45	99	0.104ab	0.229a
Arena	397	53	116	0.134b	0.292b

For BCF, values followed by same lowercase letter in each column show no significant differences for $p \geq 0.05$ according to Tukey HSD test

Prado soil. When the spiked biosolid was used, only TCS behaved similarly. For EE2, the BCF was highest for sand, followed by the Lampa soil and, to a smaller degree, the Lo Prado soil, but the small difference found was not significant. A comparison of the BCFs of TCS and EE2 that were obtained when the plants were grown in sand and soils treated with spiked biosolids, with the BCFs obtained when natural biosolids were used, showed smaller BCFs for TCS and EE2 in the soils treated with spiked biosolid. This result potentially occurred because the plants have similar limits for contaminant bioaccumulation because of some defense mechanism that prevents contaminant absorption through the plant. In addition, this could be caused by the retention of EE2 and TCS in the soil-biosolid system, which would generate results with a smaller bioavailability. This hypothesis is based on the high octanol-water partitioning coefficient of EE2 and TCS, 3.67 and 4.8, respectively, and the partitioning coefficient of organic carbon (log K_{oc}) which indicated that the compounds are mainly bound to the hydrophobic organic matter in the biosolids.

As observed in all cases, a greater BCF was obtained for plant roots because, as previously explained, roots have a high potential for lipophilic contaminant accumulation (Karnjanapiboonwong et al. 2011).

In the case of BCF for plant shoots, higher values were obtained for EE2 than for TCS in the sand and soil, which could be accounted for by the value of the octanol-water partitioning coefficient (K_{ow}) of the compounds under study because EE2 has a smaller K_{ow} than TCS. This difference allows for greater mobility and transport of EE2 to shoots due to its higher solubility in water. On the other hand, TCS has a greater tendency to be adsorbed on soil, which results in a smaller amount of available compound for uptake by the plant (Karnjanapiboonwong et al. 2010a, b). The greater the solubility of the organic compounds in water, the more readily they translocate to the plant shoot (Stevens et al. 2009). The smaller lipophilicity of EE2 is expressed as greater bioavailability in soil and higher translocation to plant shoots (Stevens et al. 2009). Compounds with strong hydrophobicity (high log K_{ow} values), such as TCS, generally remain in roots with limited distribution in the plant and could be adsorbed on the outer epidermis of the root, which could contribute to their great accumulation in roots (Wu et al. 2013). Studies of organic contaminants show that hydrophilic compounds are carried into the plant through the xylem and are distributed in the plant depending on hydrophilicity and that hydrophobic compounds are not readily translocated in the plant, thus remaining in the root (Simonich and Hites 1995).

EE2 and TCS adsorption

It was found that the adsorption equilibrium time between the adsorbate and the adsorbent is 24 h for both compounds, which is consistent with the other adsorption studies carried out for these compounds (Karnjanapiboonwong et al. 2010a, b; Yu et al. 2013; Durán-Álvarez et al. 2012; Ying and Kookana 2005). In addition, this result corresponds with the OECD Guidelines for the Testing of Chemicals: Test No. 106 (2000) recommendations for adsorption-desorption studies using the batch equilibrium method.

To assess the effects of organic matter addition on TCS and EE2 retention by incorporating biosolids into soils, studies of compound adsorption were carried out in soils with and without biosolid application. The soil samples and soil-biosolid ratio were obtained from a study of the bioavailable fraction of the compounds in wheat plants. Figures 3 and 4 show the adsorption isotherms for both compounds in the Lampa and Lo Prado soils with and without biosolid addition. In the case of TCS, the application of biosolids to the soil increased TCS adsorption. A similar but smaller increase was observed for EE2. Hence, the adsorption of these compounds on soils would depend on an increase in organic matter and on the type of soil. According to Wu et al. (2009a, b), the increase in organic matter adsorption on biosolid-amended soils would mainly result from an increase in the organic matter supplied by biosolid application, where the amount of organic carbon present in soils linearly increases with biosolid amendment. Accordingly, adsorption of these compounds should be greater in the Lo Prado soil, which contains a higher amount of organic carbon, than in the Lampa soil. However, a comparison of the adsorption isotherms obtained in both soils with or without biosolid application indicates that the adsorption of both compounds is smaller in the Lo Prado soil. Organic acid adsorption on soils usually depends on pH because organic acids appear in their neutral form when the soil pH is below the compound pKa and have a stronger tendency to be adsorbed by soil organic matter than when they are in their more polar dissociated form. On the other hand, the adsorption of compounds depends not only on the soil pH and organic carbon content but also on the clay content, with greater soil clay fractions corresponding with a greater number of adsorption sites (Chen et al. 2006). In our study, the Lampa soil has a higher percentage of clay than the Lo Prado soil, which agrees with the results obtained because the Lampa soil showed higher adsorption for both compounds. In addition, these results are consistent with the results of the study described above regarding the bioavailable fraction of EE2 and TCS in wheat plants. Specifically, greater contaminant bioaccumulation occurred in the plants grown in the Lo Prado soil, and less adsorption of both compounds occurred in this soil, which caused them to be more available for plant uptake.

Regarding the type of adsorption isotherms (Sposito 2008) obtained in this study, in most cases they were similar to those of type L isotherms and were characterized by an initial slope that did not increase as the concentration of the adsorbent species in the soil solution increases. In this case, soil particles

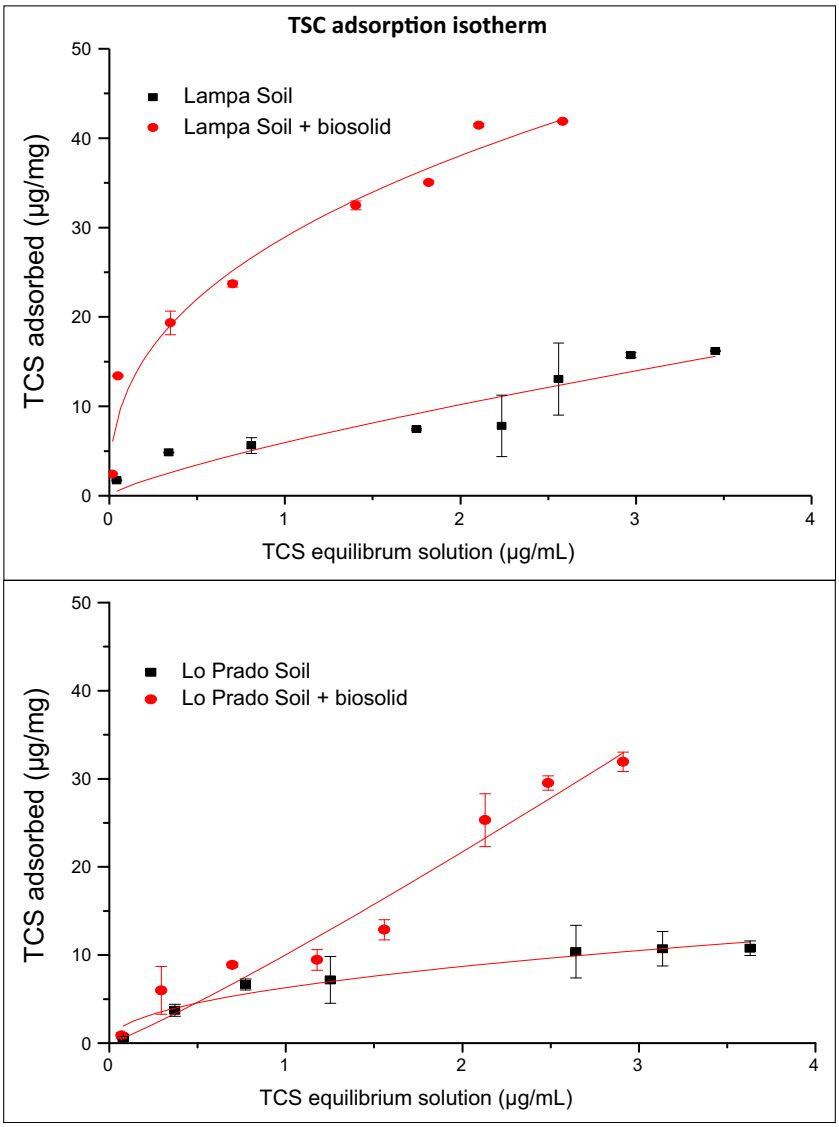

Fig. 3 Adsorption isotherms of TCS in soils Lampa and Lo Prado with and without application of biosolids. Values represent the mean ($n = 2$), and the *error bars* are given as standard deviation (±SD)

show high affinity for the adsorbate with a low level of surface coating, which would result in specific adsorption or chemisorption. The isotherms obtained for EE2 in both soils and for TCS in the Lo Prado soil with biosolid were similar to those of type C, which suggested a constant compound affinity at the different adsorption sites.

Table 4 shows details of the adsorption constants obtained for both compounds in the Lampa and Lo Prado soils. The values of the Freundlich adsorption constant (K_f) for both compounds in the biosolid-amended soils were greater than those obtained in the soils without biosolid application. The K_f values derived from the Freundlich equation reflect the adsorption affinity of the compounds in the soil and are usually associated with organic matter content, i.e., higher K_f values are related to greater organic matter contents in the soil (Yu et al. 2013; Xu et al. 2009). In the case of biosolid-amended Lampa soil, the highest K_f value was obtained for TCS adsorption, followed by EE2 adsorption on the same soil, 28.9 and 25.7, respectively. The lowest values for this constant are for TCS in the Lampa and Lo Prado soils without biosolids, 6.94 and 6.30, respectively. The values for K_d obtained for the compounds (the same as K_f) are higher in the soils treated with biosolids. A comparison of the Freundlich constant values obtained for both compounds in the different substrates shows that the highest values were obtained for the Lampa soil.

From the results obtained for K_f and K_d, it may be observed that the content of organic carbon in the soil was not the main adsorption supplier in this case because the Lampa soil had a lower organic carbon content with higher constants in the biosolid-amended soil and the highest K_f and K_d values compared with the Lo Prado soil. Furthermore, as explained above, adsorption could be directly associated with the magnitude of the soil clay fraction.

According to Xu et al. (2009), K_f values cannot be compared between samples when the obtained nonlinear factors (1/n) are very different. For the Freundlich 1/n constant, the

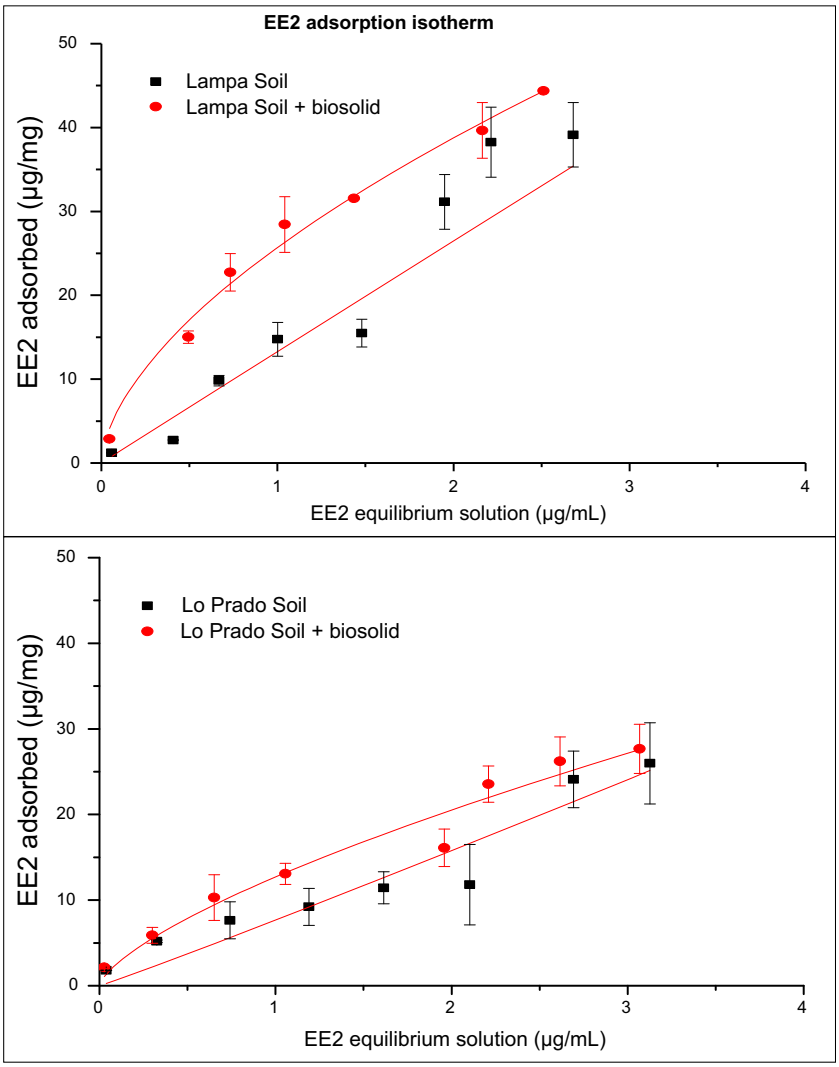

Fig. 4 Adsorption isotherms of EE2 in soils Lampa and Lo Prado with and without application of biosolids. Values represent the mean ($n = 2$), and the *error bars* are given as standard deviation (±DS)

Table 4 Adsorption of TCS and EE2 in Lampa and Lo Prado soils, treated without and with biosolids

Soil		Freundlich model			Lineal model		
		K_f[a]	1/n	r^2	K_d[b]	Log K_{oc}	r^2
EE2	LMP	13.3	1.17	0.95	15.0	3.12	0.94
	LMP + B	25.7	0.59	0.98	19.9	3.00	0.83
	LPR	7.66	1.04	0.93	7.95	2.51	0.91
	LPR + B	12.7	0.69	0.96	9.75	2.49	0.91
TCS	LMP	6.94	0.78	0.94	4.48	2.62	0.86
	LMP + B	28.9	0.39	0.97	19.3	2.99	0.63
	LPR	6.30	0.70	0.96	3.58	2.16	0.62
	LPR + B	10.0	1.11	0.95	11.0	2.49	0.95

LMP Lampa soil, *LMP + B* Lampa soil treated with biosolid, *LPR* Lo Prado soil, *LPR + B* Lo Prado soil treated with biosolid

[a] $(\mu g/g)(\mu g/mL)^n$

[b] In milliliters per gram

values obtained were from 0.39 to 1.17, and only three of the values were close to 1, which indicated that the adsorption isotherms for the compounds would not be linear and would follow the Freundlich model. This result would also be reflected in the determination coefficient values (r^2) obtained for both models because they range from 0.62 to 0.95 for the linear model and from 0.93 to 0.98 for the Freundlich model, indicating that the values were fit better by the Freundlich model.

The values determined for log K_{oc} were similar to those determined for TCS for all of the studied adsorbents, except for the Lo Prado soil (log $K_{oc} = 2.16$), and ranged from 2.16 to 2.99. For EE2, the obtained values ranged from 2.49 to 3.12 and were similar for the same soils. The highest log K_{oc} values for both compounds were obtained in the Lampa soil with and without biosolid application, which is directly related to the values obtained for K_f and K_d.

Regarding the TCS and EE2 desorption study, desorption of both compounds was very low in the Lampa soil with and

Table 5 Desorption percentage of TCS and EE2 in Lampa and Lo Prado soils, treated without and with biosolids

	Added concentration (μg/mL)	Desorption (%)[a]			
		Lampa soil	Lampa soil + biosolid	Lo Prado soil	Lo Prado soil + biosolid
TCS	0.5	0.69	ND	46.8	32.5
	1.5	5.97	ND	39.7	23.7
	3.5	3.20	1.16	57.1	28.6
EE2	0.5	7.56	0.82	12.4	4.50
	1.5	6.34	1.93	11.2	5.74
	3.5	5.53	2.58	19.8	10.4

ND not detected

[a] Percentage desorbed

without biosolid application. In the Lo Prado soil, the percentage of adsorption was higher. For both compounds, Table 5 shows that the desorption percentage was lower in biosolid-treated soils, which may be explained by organic matter hydrophobicity and results in these compounds being retained on this substrate.

In the Lo Prado soil, nearly 50% of the TCS was desorbed during the study period, and this percentage decreased by nearly half when the soil was treated with biosolids. The same result occurred for EE2, but a lower desorption percentage was obtained in the soils without and with biosolid application. In the Lampa soil, EE2 desorption was higher than TCS desorption and was very low for both compounds. These results reflect a smaller adsorption force for TCS and EE2 in the Lo Prado soil and a greater mobility of the compounds in this soil.

As explained above, the Lampa soil has a lower organic carbon content than the Lo Prado soil but a greater clay fraction (20 and 8%, respectively), which may be a relevant factor in adsorption and, in this case, compound desorption because TCS and EE2 are desorbed at a lower rate in the Lampa soil and are able to remain strongly bound to the soil colloidal fraction.

Conclusion

Our results suggest that estrogens such as EE2 and antibacterial compounds like TCS may be taken up by wheat plants and mainly accumulate in plant roots.

The bioavailability of these contaminants in wheat plant assays followed the same tendency (i.e., the concentrations of EE2 and TCS were greater in the wheat plants that were grown in sand, followed by the Lo Prado soil and the Lampa soil). The only observed differences were between the different substrates for the EE2-spiked biosolids; however, these differences were not significant ($p > 0.05$). In this study, bioavailability was directly related to the pKa value of compounds, the clay fraction, and the pH of soils rather than to the amount of organic carbon present in the soil. However, for the case of sand the absence of organic carbon could allow for greater bioaccumulation of contaminants in wheat plants.

Regarding the determination of bioaccumulation factors, a smaller BCF was obtained for EE2 and TCS when the wheat plants were grown in the soil and sand treated with spiked biosolids than when the plants were grown in the same substrates treated with natural biosolids, with smaller phytoaccumulation observed in the latter case. Possibly to obtain similar results, it would be necessary that the time of the bioassay could be greater than 30 days, so that a greater amount of these compounds contained in the soil-biosolid substrate can be absorbed by the plant.

In addition, a greater BCF was observed for the roots than for the shoots, with higher values for EE2 than for TCS in the sand and soil.

This adsorption study shows that increases in organic matter due to biosolid application result in greater TCS and EE2 adsorption in soils. In addition, the adsorption of these contaminants in soils with and without biosolid application was greater for the Lampa soil than for the Lo Prado soil, which suggests that adsorption could be directly associated with the clay content in the soils. The values obtained for K_d and K_f were higher in the biosolid-treated soils, except for EE2 in the Lampa soil because a higher K_d value was obtained in the absence of biosolids. According to the 1/n and r^2 values obtained from the adsorption isotherms, it was determined that the Freundlich model fit the data better than the linear model.

The desorption study showed that both TCS and EE2 availability is very small in the case of the Lampa soil with and without biosolid application, but would increase in approximately 50% in the cases of TCS in the Lo Prado soil. Finally, it may be concluded that the adsorption of TCS and EE2 to soils increases as the organic matter content supplied by the biosolids increases, which would decrease the bioavailability of the contaminants in wheat plants, which in some cases depends on the type of soils.

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