New biomimetic approach to determine the bioavailability of triclosan in soils and its validation with the wheat plant uptake bioassay

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HIGHLIGHTS

- We developed a new biomimetic method to estimate the bioavailability of triclosan.
- The biomimetic method was based on rotating disk sorptive extraction.
- The biomimetic approach was applied to different biosolid-amended soils.
- A good correlation was obtained between TCS content in plants and in leaching.
- Bioavailability of TCS decreases when the biosolid dose in soil increases.

ARTICLE INFO

ABSTRACT

A new biomimetic approach for triclosan (TCS) was developed based on the leaching of the analyte from different biosolid-amended agricultural soils and the subsequent extraction of the leachates, using a rotating disk sorptive extraction (RDSE) procedure. The leaching equilibrium for TCS was reached at 3 h when the ISO method (ISO/TS 21268-1:2007) was followed.

The concentrations determined by this biomimetic method were compared with the bioavailability of TCS, determined by its accumulation in the roots of wheat plants grown in the same soil–biosolid systems.

It was observed that the amount of organic matter in the soil matrix was a determining factor for mobilization of TCS. An increasing biosolid rate applied to soils resulted in a reduced mobility of TCS because the high amount of organic matter provided by the biosolid increased the hydrophobic interaction between TCS and the matrix. Similarly, increasing biosolid concentrations in the soil significantly decreased the bioavailability of TCS to the wheat plant. Thus, the bioavailability factor in wheat roots decreased from 0.22 to 0.08 for a soil having a pH of 8.2, when the biosolid rate was increased from 30 to 200 Mg ha^{-1}, respectively.

A significant correlation ($R = 0.98$) was obtained between TCS concentration in wheat plants and the proposed biomimetic methodology, indicating that the latter can predict the bioavailability in a time period as short as 180 min.

The results of this study confirm our previous findings that amending soils with biosolids is beneficial for immobilizing low polarity contaminants and helps prevent their percolation through the soil profile and into groundwater.

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1. Introduction

From an environmental perspective, the total amount of a compound in a matrix such as soil is not sufficient information for a risk assessment. The most significant fraction of a contaminant in an environmental matrix is the fraction that can be taken up or transformed by living organisms, typically called the bioavailable fraction (Semple et al., 2003). Bioavailability of a compound depends on the organism, the species, the physicochemical features of the target compound and the soil characteristics, i.e., organic matter, pH, and moisture (Van der Wal et al., 2004). The most important factors determining the amount of a chemical that is bioavailable are the transfer rate of a compound from the matrix to the living cell (mass transfer) and the consumption rate and metabolism (intrinsic activity) of the cell (Semple et al., 2003; Stokes et al., 2005).

Consequently, by this definition, bioavailability is determined by biological measurements or bioassays; however, these bioassays have constraints such as high variability (Wu et al., 2011), ethical issues, difficulty in culturing organisms (Cachada et al., 2014), and they are time consuming and expensive.

Alternatively, chemical methods have been proposed to predict the bioavailability of environmental pollutants in soils. Some studies have demonstrated that the labile or the freely dissolved fraction of a given pollutant is related to the corresponding fraction available to living organisms (Urrestarazu et al., 1998; Caicedo et al., 2011). The freely dissolved fraction refers to molecules in aqueous solution that are not bound to the matrix, or to the dissolved organic matter; this portion is more likely to be determined in media with high water content and not on a dry matrix, such as in air or dry soil (Reichenberg and Mayer, 2006). The extraction of the labile fraction may be performed using: (a) a mild solvent extractant medium, such as an organic solvent or in an aqueous solution (Kelsey et al., 1996; Liste and Alexander, 2002), (b) a complexing agent, such as a cyclodextrin solution (Cuypers et al., 2002), (c) a sorbent phase in wet soils, such as: Tenax (Cornelissen et al., 1998; Ten Hulscher et al., 2003), Empore C18 disks (Krauss and Wilcke, 2001) or (d) through the intervention of passive samplers, for instance, semipermeable membrane devices (Kelsey et al., 1996), solid phase microextraction (SPME), DGTs (Ahumada et al., 2011). These techniques simulate the capability of an organism to absorb organic pollutants similarly to a living organism. This is why these methods are called biomimetic (Cui et al., 2013). In biomimetic extractions the use of synthetic polymers in the extracting phase acts as a surrogate for the organism. The fraction accumulated by the polymeric phase simulates the bioavailable fraction (Hartnik et al., 2008), which operates on the principle of partition equilibrium (Cui et al., 2013). The time to reach this equilibrium depends on the device; usually devices coated with a polymer sorbent need less time due to a larger surface to volume ratio (Van der Wal et al., 2004). In general, for these passive sampler devices the aqueous-leaching of the pollutant is integrated to the extraction of the pollutant into the device. In other words, the leaching equilibrium can compete with the extraction equilibrium. On the other hand, sequential extraction methodologies have also been reported (Caicedo et al., 2011), in which interference between equilibria are avoided.

On the basis of these considerations, a biomimetic approach, in which the bioavailability of organic pollutants in agricultural soils amended with biosolid was estimated, was developed in this study. The two agricultural soils studied belong to the series Taqueral and Cuesta Vieja and are from the Metropolitan Region of Chile. The biosolid was obtained from the main waste water treatment plant of the region.

This approach combines a leaching procedure for TCS in an aqueous solution with the subsequent quantitative determination of the analyte in the leachate through the rotating disk sorptive extraction (RDSE) technique. Triclosan (TCS) was used as a model hydrophobic compound because of its importance as emerging pollutant (Bester, 2003; Chu and Metcalfe, 2007; Cha and Cupples, 2009; Sanchez-Prado et al., 2010; Chen et al., 2011).

The RDSE technique was developed in 2009 for the determination of different pollutants from water samples (Richter et al., 2009, 2011; Giordano et al., 2011; Manzo et al., 2012) including TCS and methyl-triclosan (MTCS) from waste water (Jachero et al., 2013).

Considering that the only way to determine if a compound is bioavailable is to employ a living organism (Lanno et al., 2004), in this study, trials with wheat plants cultivated in an identical soil–biosolid mixture were performed to assess the feasibility of the biomimetic method. To measure the degree of significance of the association between the two methods, a weighted regression model was applied, using an iterative least squares approximation known as bivariate least square (BLS), because BLS considers the errors associated with two variables (Del Río et al., 2001). In contrast, the ordinary least square (OLS) regression method assumes that uncertainty is only in the dependent variable.

2. Experimental

2.1. Reagents

A Millipore Milli-Q PLUS ultrapure water system (Billerica, MA, USA) was used throughout the experiment. TCS and MTCS (both 99.5% purity) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). A standard stock solution of the analyte was prepared in methanol (GC–MS/pesticides grade analysis, Fisher Scientific, Fair Lawn, NJ, USA). Hexachlorobenzene (HCB, 99.5% purity) was used as an internal standard and was purchased from Dr. Ehrenstorfer GmbH. Labeled $^{13}C_{12}$-TCS (50 mg L^{-1}), purchased from Wellington Laboratories (Ontario, Canada), was used as a surrogate standard. Nitrogen 5.0 and helium 5.0 were purchased from Linde (Santiago, Chile) and were used in the final extract evaporation and as the chromatographic carrier gas, respectively. Ethyl-acetate, acetone (both HPLC grade, 99.8% purity), sodium chloride (99.5% purity), anhydrous sodium sulfate (99% purity) and calcium carbonate (99% purity) were purchased from Merck (Darmstadt, Germany). The PDMS phase was prepared from a Sylgard 184 silicone elastomer kit (Dow Corning, MI, USA) according to the manufacturer's recommendations. A 0.1 M citrate buffer (disodium citrate, Merck) was adjusted to pH 4.0 with hydrochloric acid (Merck). N-methyl-N-(tertbutyldimethylsilyl) trifluoroacetamide (MTBSTFA) was provided by Sigma Aldrich (Milwaukee, WI, USA) and was used as a derivatizing agent. Sorbents for solid phase extraction were Florisil® (60–100 mesh), and C18 (70–230 mesh) from Sigma–Aldrich.

2.2. Instruments and software

A Thermo Scientific gas chromatograph model Focus (Milan, Italy) coupled to a mass-selective detector (Thermo Fisher Scientific model ISQ, Austin, TX, USA) was used for final determinations. The fused silica capillary column used was a Restek RTX-5MS (Bellefonte, PA, USA – 30 m × 0.25 mm id; 0.25 μm film thickness) coated with 5% phenyl–95% methylpolysiloxane. Two microliters of sample extract were injected into the gas chromatograph using the splitless mode. The injector temperature was 250 °C. The initial column temperature was 100 °C (1 min) and was increased to 300 °C at 10 °C min^{-1}. A constant flow of 1.0 mL min^{-1} of helium as a carrier gas was used. The solvent delay was 7 min. A dwell time of 0.1 s was employed for each m/z. The MS transfer line was maintained at 250 °C, and quantifications were based on calibration with the standard analyte using mass spectrometric parameters in selective ion monitoring (SIM) mode.

2.3. Soil and biosolid samples

Two soil samples of composed surface soil (0–10 cm) were taken from an agricultural land area near Santiago in Central Chile. At each site, five replicates were obtained (one from each corner and one from the center of the plot) with a stainless-steel hand auger fitted with a plastic liner. The subsamples were mixed, reduced, and processed. The resultant samples were air-dried and passed through a 2-mm mesh-size polyethylene sieve. The soils were classified in the Mollisol order, and they were identified as Taqueral (6309.5 km Lat.; 331.4 km Long. UTM) and Cuesta Vieja (6292.9 km Lat.; 317.9 km Long. UTM).

Samples of anaerobically stabilized sludges or biosolids were collected from monofills at Santiago de Chile sewage treatment plants.

The soil used in this study did not contain detectable quantities of TCS. The biosolids contained 12.5 ± 0.5 mg kg^{-1} TCS, which was determined by matrix solid phase dispersion (MSPD) according to the method described by Sánchez-Brunete et al. (2010). Biosolids containing higher concentrations of TCS were achieved by spiking the analyte in the matrix, using the following procedure: a 500 g portion of biosolid was placed in a separate 500 mL round flask, and an additional TCS concentration (approximately 10 mg kg^{-1}) was added using the commercial formulation Irgasan™. The samples were covered in acetone, evaporated in a Rotavapor® R-134 (Buchi) at 200 rpm for 48 h and aged for 5 d at room temperature in darkness.

2.4. Preparation of soil–biosolid samples

Portions of each soil were mixed with different fractions of biosolids (at a rate of 30, 60, 90 y 200 Mg ha^{-1}). The same mixtures with the soils were made using the spiked biosolid. The samples were homogenized and aged for one week at room temperature under field humidity conditions.

2.5. Procedure for the biomimetic method

Portions ($n = 3$) of 13 g of each soil–biosolid mixture were suspended in 25 mL of 0.001 M CaCl$_2$ in 30 mL amber glass bottles fitted with Teflon stoppers, as per ISO/TS 21268-1:2007. Suspensions were stirred at 150 rpm for 3 h, after which the supernatant was filtered, and the concentration of the analyte leached was determined by extraction with RDSE. GC–MS analysis according to the method described by Jachero et al. (2013) followed. Briefly, a volume of 25 mL of the leachate was poured into a beaker and adjusted to pH 4.0 with 0.1 M citrate buffer. Surrogate standard ($^{13}C_{12}$-TCS) at 5 µg L^{-1} and NaCl at 20% (w/v) were added. The rotating disk containing the PDMS phase was placed inside the beaker, and the disk was rotated at 1250 rpm for 80 min at room temperature. After extraction, the disk was placed into a 10 mL beaker containing 5 mL methanol as a desorbing solvent and was stirred for 30 min at 1250 rpm. The methanol extract containing the concentrated analyte was then evaporated under an N$_2$ stream to dryness and re-dissolved into 1 mL of ethyl-acetate. A volume of 500 µL of the extract was derivatized for 45 min at 80 °C by adding 50 µL of MTBSTFA. Prior to injection, 10 µL of 5 mg L^{-1} HCB was added as an internal standard, and the analyte concentration was determined by GC–MS.

Considering three replicates of biosolid-amended soils and two different soils, including the mixtures with spiked biosolids, the number of trials was 48 (two soils, four biosolid rates, two biosolids, three replicates).

2.6. Wheat plant cultivation for the bioavailability study

One hundred and fifty wheat seeds (*Triticum aestivum*) were planted in pots that contained 200 g of different amended soils on 300 g of quartz sand. The pots were cultivated in an environmentally controlled cultivation site and watered every other day with deionized water. The plants were grown under a cycle of 14 h d at 25 °C and 10 h nights at 20 °C. Three replicates were used for each soil treatment with different amounts of biosolid, for a total of 48 plants. The cultivation period was 30 d. After this period, the wheat plants were harvested, and soil samples collected. The plant samples were thoroughly washed with deionized water to remove soil particles. TCS was measured in the plant samples; the roots and aerial parts were analyzed separately. TCS was extracted from the plants by matrix solid phase dispersion (MSPD) by following the method proposed by Sánchez-Brunete et al. (2010).

3. Results and discussions

Given the widespread use of personal care products containing TCS, concentration levels of TCS found in biosolids from Chilean wastewater treatment plants are high and similar to those found in biosolids of other countries (Table 1).

Compared with other emerging pollutants in biosolids, TCS is one of the compounds found in higher concentration in this matrix (Liu et al., 2009; Sabourin et al., 2012). The mobilization of this compound to other environmental compartments such as soil and water has been frequently observed (Lindström et al., 2002; McAvoy et al., 2002; Singer et al., 2002), which can promote the development of resistant organisms and cause adverse effects on ecosystems. Moreover, it is known that in biologically active media TCS can biodegrade to MTCS. The concentration found of MTCS in the biosolids used in this study was 0.17 ± 0.03 mg kg^{-1}.

Because low polarity of TCS, it tends to accumulate in the organic matter of the biosolids (Lozano et al., 2013, Langdon et al., 2013). However, when a biosolid is applied as a soil amendment to improve soil characteristics, mobility of the pollutant through the soil solution to the biota can be induced.

In this context, to assess the bioavailability of TCS in soils, its mobility can be determined by a biomimetic method combining a leaching procedure in aqueous media for TCS, followed by TCS determination in the leachate using a rotating disk sorptive extraction (RDSE) technique.

The leaching profile of TCS in the different soil–biosolid mixtures was determined following the method given in ISO/TS 21268-1:2007. The leaching behavior was similar in both soils for all biosolid rates, similarly to that previously observed for lindane in Chilean soils (Caicedo et al., 2011). The leaching time profiles, in both soils, at a representative biosolid rate of 90 Mg ha^{-1}, are shown in Fig. 1.

The equilibrium time for both soils is between 2.5 and 4.5 h. A leaching time of 3 h was selected for the further experiments.

The leachable fraction (LF) of TCS for each soil–biosolid system under study was determined by RDSE and GC–MS as:

$$LF\ (\%) = \frac{\text{mass of TCS in } \mu g \text{ in the leaching}}{\text{total mass of TCS in } \mu g \text{ in the soil—biosolid}} * 100 \quad (1)$$

The leaching extent is influenced by the characteristics of the soil depending on its texture, homogeneity, porosity, organic matter content, and also by the physicochemical features of the compound, such as charge and molecular size (Sparks, 1995). Fig. 2A

Table 1
TCS content in biosolid from different countries.

Country	TCS, mg kg^{-1}	Reference
Madrid, Spain	2.98	Sánchez-Brunete et al. (2010)
Santiago de Compostela, Spain	2.64	González-Mariño et al. (2010)
Melbourne, Australia	16.79	Ying and Kookana (2007)
Ontario, Canada	11.55	Chu and Metcalfe (2007)
Leipzig, Germany	0.28	Casas Ferreira et al. (2011)
Ohio, USA	15.60	McAvoy et al. (2002)
Germany	8.80	Bester (2003)
Michigan, USA	7.06	Cha and Cupples (2009)
USA	32.90	Kinney et al. (2006)
USA	20.00	Heidler and Halden (2007)
Denmark	15.60	Chen and Bester (2009)
Santiago, Chile	12.5 ± 0.5	This work
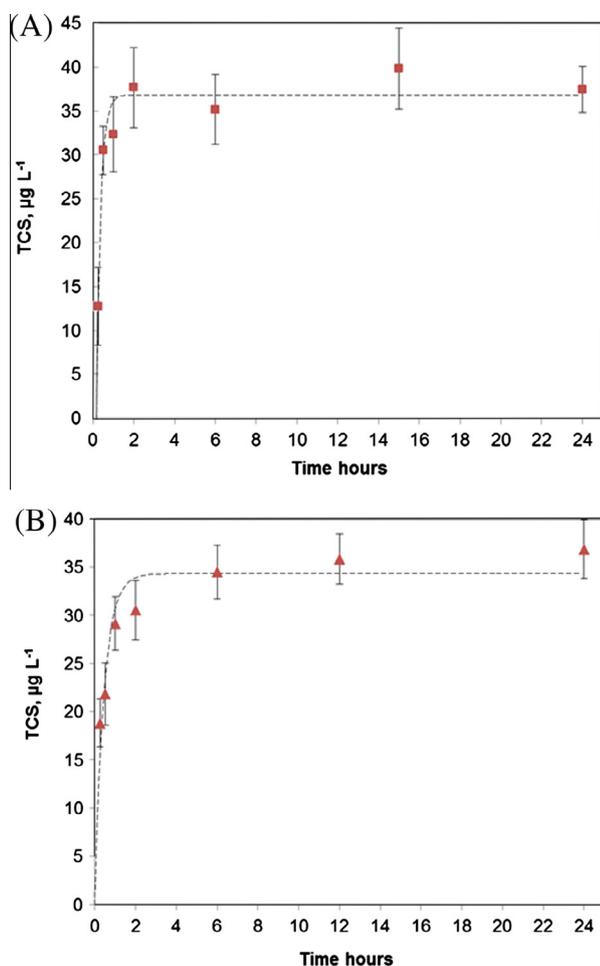
Fig. 1. Leaching profile of TCS in Taqueral (A) y Cuesta Vieja (B) soils, (*n* = 3).

Fig. 2. Leachable fraction of TCS in amended soils respect to the biosolid rate. (A) Soil–biosolid mixtures and (B) soil–spiked biosolid mixtures (*n* = 3).

shows that the native compound present in the biosolid is more strongly retained in the matrix than the spiked compound (Fig. 2B) and also shows that the leaching fraction decreases as the rate of biosolid increases in the mixture.

The results obtained in these leaching tests demonstrate that a fraction of TCS in the soil–biosolid mixture is transferred to the aqueous extract. Although this fraction is low, from an environmental perspective is relevant because it is a major route of entry of TCS in living organisms and other environmental compartments.

Despite the total increase in TCS when the biosolid rate was increased in the mixture, as a result of TCS present in this matrix, the hydrophobic organic matter also increased, providing more active sites for immobilization of TCS. This interaction restricts the free leaching (or lability) of the compound, which confirms that amending a soil with biosolids contributes to the immobilization of TCS and helps prevent its percolation through the soil profile and into the groundwater, analogous to the lindane behavior in soils reported previously (Caicedo et al., 2011). Regarding MTCS, it was not detected in leaching test due its hydrophobicity and its low concentration in the soil–biosolid mixture.

Given the low polarity of TCS and MTCS, their primary interaction is with the hydrophobic organic matter contained in the soil–biosolid mixture, while the interaction with the inorganic components is negligible.

Taqueral and Cuesta Vieja soils have a pH of 8.2 and 6.5, respectively, which also plays an important role in the mobility of TCS (Ribeiro et al., 2002; Xu et al., 2009; Lyndall et al., 2010) because the pKa of TCS is 7.8. Because of this, a higher mobility is expected
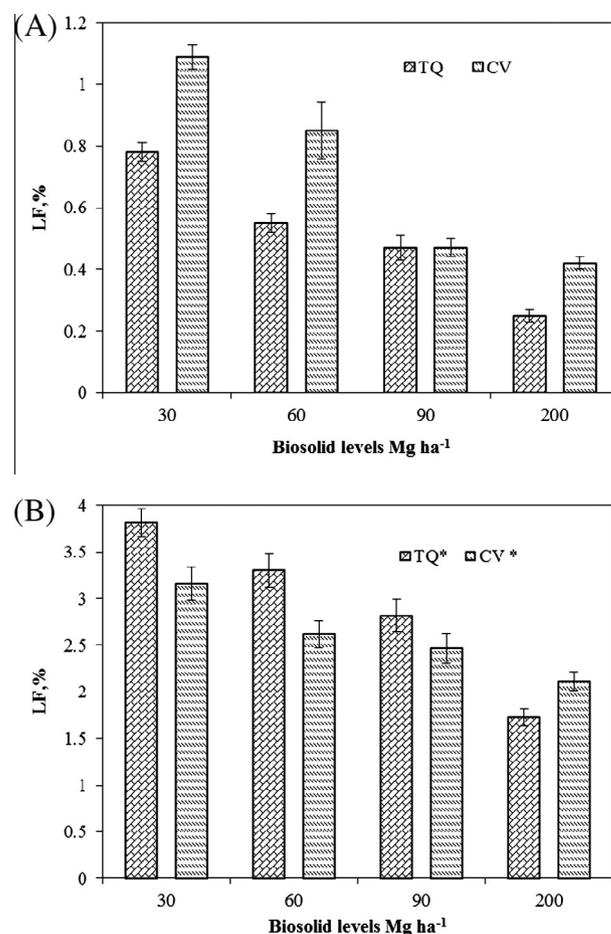
in Taqueral soil during leaching. However, mobility is also influenced by the organic matter (OM) content of the soil. Taqueral soil has an OM content (5.9%) significantly higher than Cuesta Vieja soil (3.3%), favoring retention of TCS. Fig. 2A and 2B indicates that mobility is more influenced by the lower OM content because, in general, a higher concentration of TCS was leached from the Cuesta Vieja soil. Conversely, in soils amended with biosolids enriched with TCS, the effect is opposite to that described above because mobility is higher in the Taqueral soil. Under these conditions, it is likely that the spiked analyte–matrix interaction is weaker than the interaction with the native analyte, and the effect of the soil pH predominates.

Taking into account the additional time needed for the RDSE procedure (40 min), the entire time for the proposed biomimetic method is significantly less than the times for other methods previously reported. For instance, when Empore disks were used for the analyte pentachlorophenol, the equilibrium was reached after two weeks, and a larger sample volume was employed (Verbruggen et al., 2000).

Additionally, the rotating disk used as an extraction device in this biomimetic approach did not alter the concentration of the labile fraction of the contaminants because the extraction process was performed sequentially to the free leaching of the contaminants in water. This is an advantage over other extraction devices in which leaching of the contaminant into water is integrated with the extraction into the extraction device because analyte depletion can occur during the process, disrupting the equilibrium between the bound and unbound compound in the matrix (Urrestarazu et al., 1998; Broeders et al., 2011; Gómez-Eyles et al., 2012). The

effect of the integration of both processes (leaching plus RDSE) will be studied in the future.

The bioavailable fraction (BF) of TCS in wheat plants was calculated with the following equation:

$$BF\,(\%) = \frac{\text{mass of TCS in } \mu g \text{ present in the root of the plant}}{\text{total mass if TCS in } \mu g \text{ in soil—biosolid contained in the pot}} * 100 \tag{2}$$

The total mass of TCS in both biosolid and plant roots was measured by the method of Sánchez-Brunete et al. (2010). Taking into consideration that MTCS concentration in plant roots was very low (TCS/MTCS concentration ratio about 100) no mass balance was carried out. These traces of MTCS found in plant roots can be derived from the soil–biosolid mixture or from the biodegradation of TCS in the plant.

Fig. 3A and 3B indicates that, similarly to the results observed in the leaching test, native TCS present in biosolid is less bioavailable than spiked compound added to the matrix. In addition, TCS absorbed by plant roots shows a similar pattern, decreasing with increasing doses of biosolid, a trend observed in both soils.

An increase in biosolids, effectively increases the plant biomass, however the concentration of MTCS in the root does not show significant differences. A more detailed study is currently performed and the results will be reported elsewhere.

As shown in Figs. 2 and 3, bioassays generally exhibit more variability with respect to the leaching tests, most likely due to the biological variability produced by the continued root growth, which results in heterogeneity on contact with the soil–biosolid matrix.
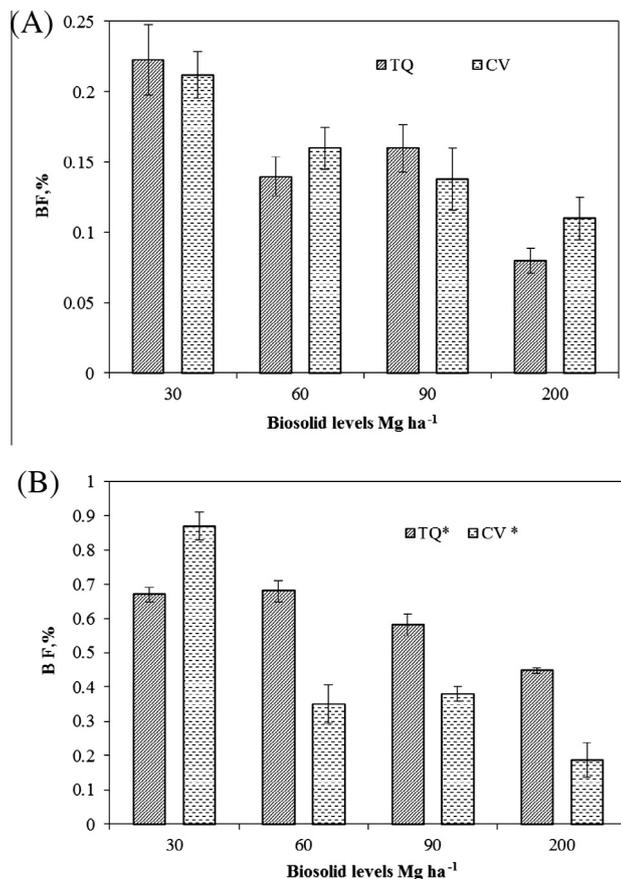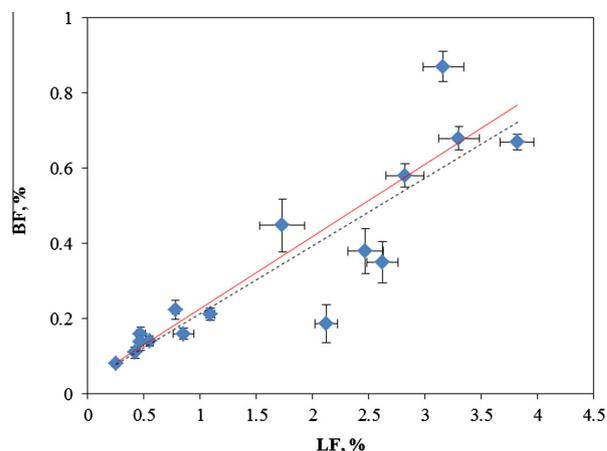

Fig. 4. Relationship between bioavailable fraction of TCS and leaching test through simple linear correlation (R) (n = 3). Segmented line (OLS), continuous line (BLS).

Table 2
Parameters of correlation analyses.

Model	Intercept	Slope	Correl. Coef.	R^2
BLS	0.034 ± 0.020	0.191 ± 0.017	0.98	96.04
OLS	0.034 ± 0.049	0.180 ± 0.024	0.79	62.41

3.1. Comparison between the bioassay and biomimetic methods (bioavailable and leaching fraction)

Fractions LF and BF, determined according to Eqs. (1) and (2), respectively, were compared by applying the BLS and OLS correlation models. Fig. 4 shows the regression lines constructed, by associating the two soils prepared with different doses of biosolids.

As can be observed in Table 2, the uncertainly in the regression coefficients was lower and the correlation index was higher for the BLS model. In the BLS model the regression coefficients and the correlation indexes were a function of the weighted value of %LF y %BF, giving a higher weight to values with lower dispersion (the range of lower concentrations) (Del Río et al., 2001). This allows future estimations of %BF with lower bias for values higher than 2% of LF, which in turn gives the model a higher predictive capacity for all intervals of studied concentrations.

In this context, the equation to predict the BF is: BF = 0.191FL + 0.034 (Table 2). From this equation is possible to estimate the BF in times as short as 3.6 h, avoiding a 48-d bioassay.

4. Conclusions

A new biomimetic method to estimate the bioavailable fraction of TCS was developed and validated by a bioassay with wheat plants. This approach coupled the leaching process with subsequent RDSE. A high degree of linear correlation between the leachable fraction and the bioavailable fraction was found, confirming that this method was applicable to soils amended with biosolids. The most important characteristics of this method compared to other reported biomimetic methodologies are that it has the shortest equilibration time (approx. 3 h) and uses small amounts of sample. In this approach difficulties associated with variables and *in vivo* tests are avoided.

It was observed that the amount of organic matter in the soil is a determining factor for the mobilization of TCS. Thus, results obtained in this study confirm our previous findings (Caicedo et al., 2011) that amending soils with biosolids is beneficial for immobilizing low polarity contaminants and helps prevent its percolation through the soil profile and into the groundwater.

Fig. 3. Bioavailable fraction of TCS in plant roots respect to the biosolid rate. (A) soil–biosolid mixtures and (B) soil–spiked biosolid mixtures (n = 3).

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