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RESEARCH ARTICLE

Released fraction of polychlorinated biphenyls from soil–biosolid system using a leaching procedure and its comparison with bioavailable fraction determined by wheat plant uptake

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Abstract The bioavailability of polychlorinated biphenyls (PCBs) in soils amended with biosolids was estimated using an aqueous leaching process of the compounds combined with rotating disk sorptive extraction (RDSE), and compared with bioavailability determined through of PCB absorption in wheat plants growing in the same soil–biosolid matrix. The matrices consisted of soil amended with biosolids at doses of 30, 90, and 200 Mg/ha, which increase concomitantly the organic matter content of the matrix. Considering that PCBs were natively absent in both the biosolids and soil used, the compounds were spiked in the biosolids and aged for 10 days. For each biosolid dose, the aqueous leaching profile was studied and equilibrium time was calculated to be 33 h. The leaching fractions determined by RDSE, considering total PCBs studied, were 12, 7, and 6% and the bioavailable fractions absorbed by the wheat root were found to be 0.5, 0.3, and 0.2% for 30, 90, and 200 Mg/ha doses, respectively. Both fractions leachable and bioavailable decrease with both increasing hydrophobicity of the compound (Kow) and increasing in the biosolid dose. It was found that both fractions (leaching and bioavailable) correlated according to the bivariate least squares regression, represented by a coefficient of correlation of 0.86. Therefore, the application of the chemical method involving a leaching procedure is an alternative to estimate the bioavailable fraction of PCBs in wheat plants in a simpler and in a shorter time.

Keywords Bioavailability · Leaching · Biomimetic method · Rotating disk sorptive extraction · PCBs

Introduction

It is known that organic pollutants can interact with diverse strength with the components of a soil matrix. Taking into account that living organisms cannot absorb the fraction of them strongly bound to the soil matrix, the total concentration of a compound in soil, determined by exhaustive extraction, does not reflect the biological effect that contaminants may present in biota, overestimating the levels of bioavailable concentration (Cornelissen et al. 2001). In addition, it has been reported that concentration measured after exhaustive extraction of the contaminant does not correlate with the fraction of pollutant which is absorbed by the biota (bioavailable fraction) (Kelsey et al. 1997). When a pollutant is weakly bound to a soil matrix, it can be in a potentially available or bioaccessible state (Cachada et al. 2014; Semple et al. 2003), which can be freely dissolved in the soil solution and feasibly to be captured by the biota. This fraction is a good indicator of the potential risk of chemicals (Naidu et al. 2008), and also is the most important fraction from the environmental perspective (Tao et al. 2006; Wang et al. 2013). Bioavailability is a complex process in which influencing factors such as biological characteristics of living organisms, physicochemical properties of the compounds, characteristics of the matrix, and contact time of the compound with the matrix (Mehler et al. 2011); as a consequence of this last factor, the bioavailability of a hydrophobic organic substance is reduced with time when

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it is bound to suspended particles or sediments (Sijm et al. 2000; Wong and Bidleman 2010).

While the most appropriate tool for assessing the bioavailability of pollutants is through bioassays, because they combine the interaction between the matrix, the compound, and the living organism, they consume a significant time and resources (Cachada et al. 2014) and the complex field studies adding other requirements, such as maintenance and availability of space for implementation.

In this context, the current trend in this field of research has been focused on the development of chemical methods to evaluate simply and rapidly the bioavailability of a compound, simulating the uptake effect of chemical, similar to what a living organism does (Khan et al. 2012). These methods, called biomimetic, allow a selective partition and/or adsorption of the analytes to a surrogate phase (Ehlers and Loibner 2006; Hartnik et al. 2008). Such methods are based on the measurements of a fraction of the contaminant present in the soil, assessing alternatively (a) the fraction of contaminants leached using a mild solvent, (b) the fraction of contaminants passively sorbed on hydrophobic polymers, or (c) the fraction of contaminants dissolved in the interstitial water. All these methods, however, show several limitations; on the one hand, in both mild solvent extraction and passive methods, the depletion of organic pollutants in the soil phase can be important (Krauss and Wilcke 2001); consequently, this condition leads specific requirements regarding the volume ratio of the involved phases to keep depletion at a negligible level (Verbruggen et al. 1999). On the other hand, methods based on separation of pore water from the solid matrix is unsuitable for widespread use in the routine analysis because they require large sample volumes (Hawthorne et al. 2009).

The use of aqueous media for leaching of contaminants from soil can also be classified as a mild solvent system. In some cases, these methods include the use of complexing agents such as cyclodextrin (HP-βCD), although a high surplus of cyclodextrin is necessary to leach a measurable concentration of the compound and to provide a sufficient extraction capacity in biomimetic extractions (Hartnik et al. 2008). In the case of high molecular weight polychlorinated biphenyls (PCBs), they may be too large to be accommodated into the cyclodextrin cavity; thus, no effective encapsulation occurs, reducing extractability (Wong and Bidleman 2010).

Given the limitations associated with the methods described above, this study aims to estimate the bioavailability of PCBs from soils amended with biosolid, applying a method that combines the aqueous leaching of the labile fraction or the freely dissolved fraction of PCBs; this fraction is related to the bioavailable fraction uptake by living organisms, followed by rotating disk sorptive extraction (RDSE) technique. Results provided by this combined methodology were compared with those obtained by bioassays with wheat plants. This combined chemical method was previously developed by our research group to estimate the bioavailability of an emerging pollutant, triclosan, which is considerably more polar than PCBs, obtaining in such case a significant correlation ($r = 0.98$) between the chemical method and the bioassays (Jachero et al. 2015). The significance of this method is linked to the concept of green analytical chemistry, reduction in the consumption of solvents and reagents, in addition to reducing time and cost compared to other methods to evaluate the bioavailable fraction, for example, bioassays.

Using this nonexhaustive extraction technique, the process is not interfered by depletion or other pre-treatments that can change its characteristics. The foundation of the method considered that the main function of the plant roots is to absorb the pollutant dissolved in the aqueous phase of the soil; therefore, a process of aqueous leaching would be comparable to the absorption (Wang et al. 2013). Despite the extremely low water solubility of PCBs, which would be a limiting factor, it should be pointed out that these compounds can be transported to water not only as a dissolved phase but also in suspension, either adsorbed to soil colloids or associated with other solubilizing agents (Badea et al. 2014). The analytes selected for this study were some PCB congeners selected as the most dangerous by the World Health Organization (WHO) since they have similar toxicological properties to dioxins. PCBs are among the toxic organic components which can be found in sewage sludges; there are no natural sources of PCBs, they may be found in various environmental matrices such as waters, sediments, soils, and biosolids; the latter being the most commonly used, as both fertilizer complements and soil amendments (Urbaniak et al. 2016; Wyrwicka et al. 2014; Bright and Healey 2003; Katsoyiannis and Samara 2004; Frost et al.1993). These compounds arrive in these matrices through the production, use, disposal, spills, leaks, and fires of PCB containers.

Materials and methods

Reagents

Water from a Millipore Milli-Q Plus water system (Billerica, MA) was used throughout the experiment. The standards of PCBs (congeners 77, 81, 105, 114, 118, 126, 156, 157, 167, 169) were provided by Dr. Ehrenstorfer Company (Augsburg, Germany). A mixed standard solution of 10 PCBs prepared in methanol (Merck, Darmstadt, Germany) was used to spike the biosolid and for calibration purposes. A standard of hexachlorobenzene provided by Dr. Ehrenstorfer was used as the internal standard at 1 μg/mL in methanol. Methylene chloride, acetone, methanol (all GC–MS/pesticide grade), sodium chloride, calcium chloride, silica gel 60 (0.063 to 0.200 mm, 70–30 mesh ASTM) , neutral alumina (0.063 to 0.200 mm, 70–30 mesh ASTM) and sulfuric acid (95%–97%) EMSURE® were provided by Merck and used for the sample preparation. Nitrogen (purity of 99.995%) and helium (purity 99.9999%) were purchased from Linde (Santiago, Chile), and they were used in the evaporation of the final extract and as the chromatographic carrier gas, respectively. The polydimethylsiloxane (PDMS) phase was prepared from a Sylgard 184 silicone elastomer kit (Dow Corning, MI, USA) according to the manufacturer's recommendations.

Soil and biosolid characterization

The soil samples were of the series Taqueral (TQ) and obtained from the metropolitan region in Chile, located at 6309.5 km lat. and 331.4 km long. (Universal Transverse Mercator, UTM). The particle sizes analysis showed that the soil had a sandy-loam texture. Table 1 shows the chemical features of soil and biosolid; the soils had an organic carbon (OC) content of 1.4%, alkaline pH; meanwhile the biosolids had a high OC concentration, high cation exchange capacity (CEC), and neutral pH; thus, the addition of sludge cause changes of the soil chemical characteristics, due to soil–biosolid interaction.

The biosolid resulting from anaerobic digestion was collected from a wastewater treatment plant in Santiago Metropolitan Region. The biosolid was spiked with the mixed standard solution of 10 PCBs dissolved in methanol; then, 500 g of the biosolid sample was spiked with this PCB solution, to bring it to a final concentration of 2 mg/kg in the soil–biosolid mixture; the sample was evaporated in a rotary evaporator at 200 rpm for 24 h at room temperature, and then transferred to a dish and left to dry for 10 days allowing to aging the compounds. The biosolid air-dried was passed through a 2-mm sieve and mixed thoroughly into the soil at agronomic rates equivalent to 30, 90, and 200 Mg/ha the soil–biosolid mixture were incubated at 25 °C for 15 days under field capacity moisture conditions.

Leaching test and extraction of PCBs by RDSE

Portions (n = 3) of 10 g of each soil–biosolid mixture were suspended in 20 mL of 0.001 M $CaCl_2$ in 30-mL glass bottles fitted with Teflon stoppers, according to the ISO/TS 21268-1:2007 guide. Suspensions were stirred at 150 rpm for 33 h, after which the supernatant was filtered, and the concentration of the analyte leached was determined by extraction with RDSE and determination by gas chromatography with electron capture detection (GC–ECD). Briefly, a volume of 20 mL of the leachate was poured into a beaker and methanol at 20% (*v*/*v*) was added. The rotating disk containing the PDMS phase was placed into the beaker, and the disk was rotated at 1250 rpm for 3 h at room temperature. The extraction device and synthesis of PDMS was performed according to described in Richter et al. 2009.

Table 1 Properties of soil and biosolid

Parameters	Soil	Biosolid
pH	8.2	6.8
OC %	1.42	28.1
CEC cmol/kg	22.3	71.6
Texture	Sandy-loam	

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 in 1 mL of ethyl acetate. Prior to injection, 10 μL of 1 mg/L HCB was added as an internal standard and the analyte concentration was determined by GC–ECD.

Bioassay using wheat plants and determination of PCBs in roots tissues

One hundred and fifty wheat seeds (*Triticum aestivum*) were planted in pots that contained 300 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 of daytime at 25 °C and 10 h of nighttime at 20 °C. Three replicates were used for each soil treatment with different amounts of biosolid. The cultivation period was 30 days. After this period, the wheat plants were harvested. The plant samples were thoroughly washed with deionized water to remove soil particles. PCBs were measured in the roots of the plant samples after drying them at 40 °C.

The extraction of PCBs from the roots of wheat plants was carried out by ultrasound assisted extraction, according to EPA method 3635C, a sample of 0.5 g of root was placed in a centrifuge tube and 10 mL of a hexane/acetone 1:1 was added; this sample was subjected to ultrasound (15 min) and then centrifuged for 15 min at 2500 rpm; the supernatant was concentrated and a cleanup process by following the EPA method 3665A was performed. The quantification of the analytes was made by GC–ECD.

Chromatographic GC-ECD conditions

Quantification of PCBs was performed using a Hewlett–Packard gas chromatograph, model 5890 series II (Palo Alto, CA, USA), equipped with an ECD. The chromatographic column was a Restek (Rtx®-5 ms, 30 m × 0.25 mm × 0.25 μm). One microliter of sample extract was injected into the column in splitless mode; the injector temperature was 250 °C. The initial column temperature was 100 °C and was increased at a rate of 8 °C/min to 260 °C

(3 min). Helium at a constant flow rate of 1 mL/min was used as the carrier gas.

Method validation

Calibration curves were established (Table 3) considering concentrations ranging from 1 to 30 μg/L using an internal standard of concentration 10 μg/L. The response was linear over the range of concentration studied, with correlation coefficients (r) higher than 0.99; the determination coefficients (r^2) are reported in Table 3. The limit of detection (LOD) and limit of quantification (LOQ) (Table 4) were determined for each analyte from the signal-to-noise ratio, following the 3-σ and 10-σ recommendation, respectively.

The precision of the method was assessed using a water sample spiked at a concentration of 1 μg/L. The relative standard deviation was always lower than 11%; the recovery of PCBs congeners were found to be higher than 98%. It should be noted that the methodology is associated with leachates from soils amended with biosolids, so the application is performed in water samples, using wastewater, to demonstrate their analytical applicability in a complex matrix. Soil blanks were also extracted and analyzed to ensure that no other compounds were present, which may affect the uptake.

Results and discussion

To determine the leaching fraction of PCBs, preliminary studies were done to obtain the leaching profile of the contaminant from the soil–biosolid system, which is required to select the leaching time used in further experiments. Before this, the optimization of the extraction of the analytes from the leaching matrix was performed, which was based on RDSE technique.

Optimization of RDSE

Chemical and hydrodynamic parameters were optimized for the RDSE of the analytes from the aqueous phase. Regarding the sorptive phase used, we select PDMS for this study, considering previous studies by stir bar sorptive extraction (SBSE), which showed a good performance of this phase for PCBs (Benijts et al. 2001; Popp et al. 2005).

The use of matrix modifiers, such as NaCl and methanol, can affect the extraction efficiency depending on the polarity of the analytes present in water matrices (Prieto et al. 2007, 2008, 2010). In this context, the extraction of PCBs was optimized in function of the NaCl and methanol concentrations, using a central composite experimental design ($2^K + 2K + C$) with three central points. Table 2 shows the levels studied for each factor. A desirability function (Fig. 1) was applied to evaluate the best conditions of PCB extraction, from Fig. 1, a positive effect in % methanol, and a negative effect in % NaCl can be deduced. Methanol avoids that PCBs, due to their high hydrophobicity, adsorb on the vial surface and absence of NaCl avoided the "oil effect" (Prieto et al. 2010). Consequently, a 20% methanol and the absence of NaCl were selected for further experiments.

Table 2 Maximum and minimum values studied for variables

Variables	Levels		
	− 1	0	1
% NaCl	0	10	20
% MeOH	0	10	20

Based on our previous experience (Richter et al. 2009; Giordano et al. 2011), the rotation velocity of the disk was kept at 2000 rpm, which is the maximum capability of the magnetic stirred used.

Leaching profiles

Once obtained the analytical features of the method of determination of PCBs from water, it was applied to the determination of the PCBs contained in the leachates obtained from the soil–biosolid samples according to the leaching test described by ISO/TS 21268-1:2007 guide. Leaching conditions were slightly modified by adding to the leaching solution a 20% (*w*/*w*) methanol, considering the high hydrophobicity of the analytes, thus avoiding that they absorb into the vial surfaces after the leaching process. The leaching profiles (Fig. 2) were obtained considering the soil sample amended with 90 Mg/ha of biosolid (Caicedo et al. 2011). An exponential function (ExpDec1) was used in the fitting ($y = A1*\exp(-x/t_1) + y_0$) from Origin Pro 8a program. According to the adjustment, a leaching time of 33 h was selected for all samples (Fig. 2); it should be clarified that in the present study, the compounds were spiked to the matrix (2 mg/kg of each PCB), because they were not present in the native form.

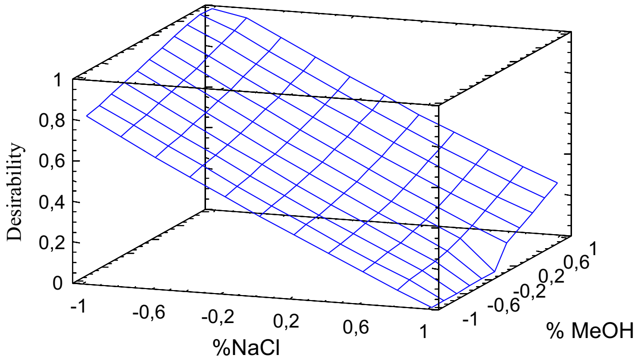


Fig. 1 Response surface estimated for the extraction of PCBs from aqueous matrices

Table 3 Regression equation for calibration curves

	PCBs									
	77	81	118	114	105	126	167	156	157	169
Slope	0.0124	0.0036	0.0236	0.0266	0.0148	0.0164	0.0584	0.0248	0.0261	0.0132
Intercept	0.0201	0.0068	0.0467	0.0432	0.0241	0.0223	0.0846	0.0444	0.0108	0.0143
r^2	0.9920	0.9897	0.9894	0.9804	0.9956	0.9933	0.9947	0.9894	0.9807	0.9965

The physical and chemical properties of PCBs vary from one congener to another (Danis et al. 2006; Huang and Hong 2002; Wong and Bidleman 2010; Badea et al. 2013); in this context, it was observed that tetrachlorinated congeners (PCB 77 and PCB 81) offer a higher extent of leaching, followed by the pentachlorinated (PCB 105, PCB 114, PCB 118, PCB 126) and finally the hexachlorinated congeners (156, 157, 167, 169). Figure 3 shows the concentrations obtained by RDSE of the different PCBs in the leaching from the soils amended with three different biosolid doses. The PCB concentration increased, due to the concomitant increase of the PCBs mass in the soil–biosolid mixture.

According to Fig. 3, there is a fraction of PCBs that is weakly bound in the organic matter and therefore was mobilized to the aqueous phase. The highly nonpolar PCBs have to be strongly absorbed in the organic phase of the soil, becoming less available in the aqueous medium. The leaching behavior of PCBs is controlled by a number of factors: OC content, pH value, and CEC; these soil properties have a fundamental role in retarding the movement of organic compounds; some PCB congeners may not have enough time to get incorporated into the matrix, having a different leaching behavior, such as PCB-169.

The different mobility from the soil observed for these compounds can be correlated with their water solubility (S) and water-octanol partition coefficient (log K_{ow}) finding correlations with determination coefficients (r^2) > 0.5 in both cases (Fig. 4a, b).

Table 4 Limit of detection and limit of quantification for PCBs

Analyte	LOD (μg/L)	LOQ (μg/L)
PCB 77	0.06	0.20
PCB 81	0.16	0.52
PCB 105	0.05	0.15
PCB 114	0.03	0.09
PCB 118	0.03	0.09
PCB 126	0.05	0.18
PCB 156	0.03	0.09
PCB 157	0.03	0.11
PCB 167	0.01	0.04
PCB 169	0.07	0.22

The higher leachability of PCBs containing a lower chlorine content can be favored also by the interaction with the dissolved organic matter (DOM) associated with the soil-biosolid matrix (Badea et al. 2014); however, this DOM should mitigate the effect of organic pollutants reducing their free concentration in solution and consequently the accumulation in organisms (Song et al. 2010). In addition, PCBs can be transferred to the water not only as a dissolved compound but also as a suspended one, either sorbed on mobile soil colloids or in an emulsion with other solubilizing agents (Adeel et al. 1997).

The total amounts leached (Σ 10 PCB) for 33 h were 12, 7, and 6% for 30, 90, and 200 Mg/ha of biosolid doses, respectively; a gradual decrease was observed in the leachable fraction, depending on the dose of biosolids (Fig. 4a, b), due to the affinity of organic matter with the hydrophobic organic pollutants and the physicochemical properties of the matrix (Tao et al. 2006; Pu et al. 2006. Badea et al., 2013). The leachable fraction was expressed as percentage (% *w*/*w*) and determined from the ratio between the mass of PCBs present in the leached extracts and the mass of PCBs present in the soil–biosolid mixture.

Bioassays

Generally, methods reported in the literature for prediction of bioavailability are validated with bioassays in animal organisms like earthworms (Krauss et al. 2000) or aquatic organisms (Hallgren et al. 2006; Verweij et al. 2004). Other studies focus validation on plants, where it has been demonstrated that the application of tools to predict bioavailability have a significant linear relationship with the concentrations of PCBs accumulated in the roots of plants (Wang et al. 2013). In this study, we performed bioassays using wheat plants, considering wheat as one of the most important crops of economic value in the world (Song et al. 2010). In Fig. 5, the concentrations of PCBs in wheat roots at 30 days of culture are shown. As expected, the concentration increases with the biosolid doses. When the concentrations of the different congeners were compared, a clear pattern is observed, in which PCBs with fewer chlorine atoms (77 and 81) have increased uptake by the roots, contrasting the compounds penta- and hexachlorinated which are more strongly

Table 5 Features of reported methods used to predict bioavailability of PCBs

Technique	Phase	Time (days)	Organism	Reference
Passive sampling	TENAX	2	Oligochaetes (*Limnodrilus hoffmeisteri*)	Kraaij et al. 2002
Passive sampling	TENAX	0.5–4	Oligochaete, (*Lumbriculus variegatus*)	Trimble et al. 2008
Matrix SPME	PDMS	14–28	Oligochaete, (*Lumbriculus variegatus*)	Trimble et al. 2008
Solid phase extraction	C_{18}	15	Earthworms (*Lumbricus terrestres L.*)	Krauss and Wilcke 2001
Passive sampling	XAD-4 Resin	20	Bivalve (*Yoldia limatula*)	Lamoureux and Brownawell 1999
Passive sampling	TENAX	1	Oligochaete (*Lumbriculus variegatus)*	Mackenbach et al. 2012
Passive sampling	TECAM	14	Plant (*Brassica chinensis L. and Daucus carota*)	Wang et al. 2013
Leaching-RDSE	PDMS	1.4	Plant (*Triticum aestivum*)	This work

linked to the organic matter of soil–biosolid system and are less available to be taken up by plants (Zhu et al. 2015). The relationship between the bioavailable fraction with Log K_{ow} and the Log S of the compounds is presented in Fig. 6a, b.

The bioavailable fraction (BF) was expressed as a percentage (% *w*/*w*) and calculated by the mass ratio between PCBs present in the root and the total mass of PCBs present in the soil–biosolid mixture. The total bioavailable fractions (Σ 10 PCBs) absorbed

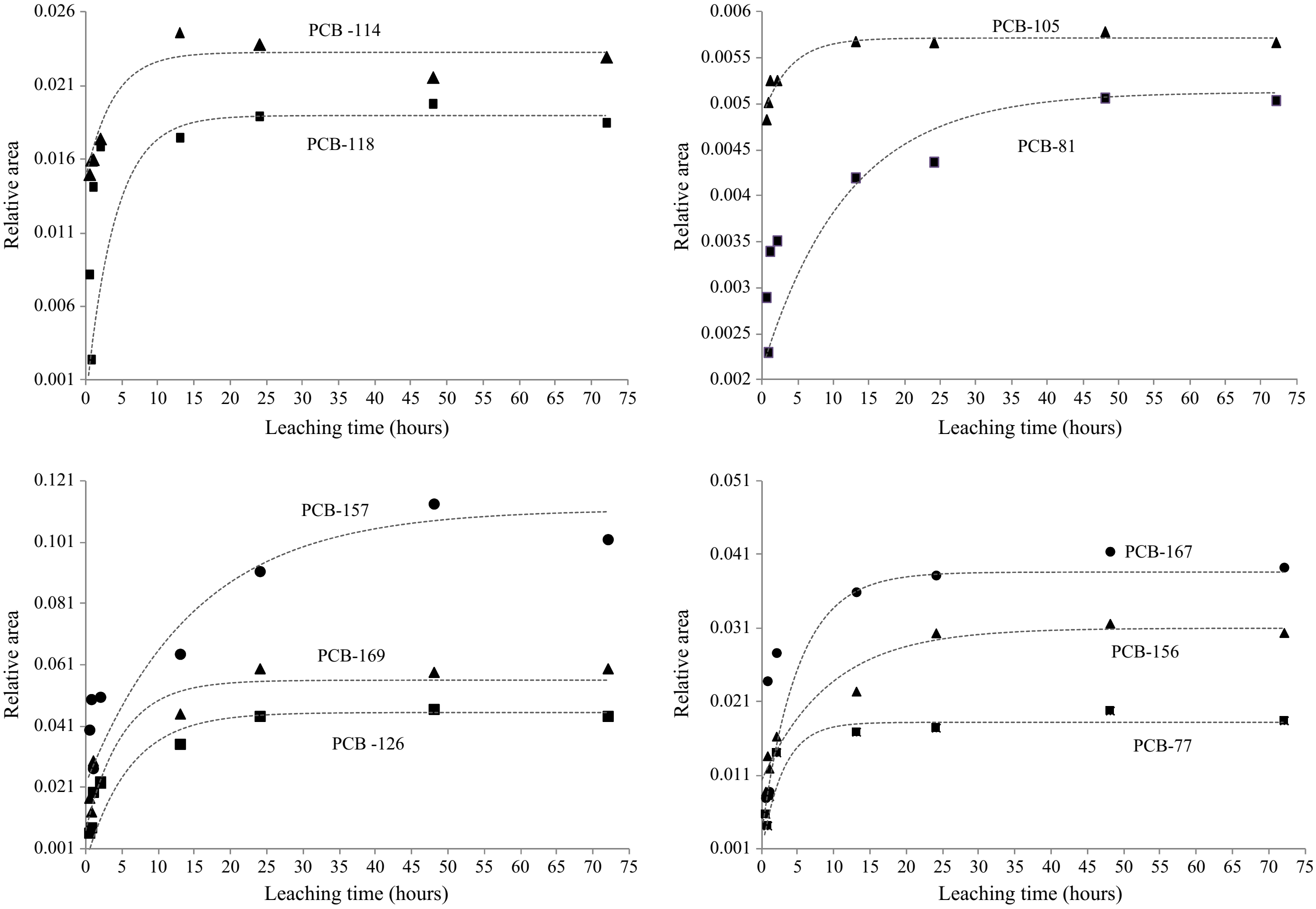


Fig. 2 Leaching profiles for each PCBs from soil–biosolid mixture. The relative area is the ratio of the analyte peak area to the internal standard peak area, in dashed black line. The exponential fitting (*ExpDec1 function*)

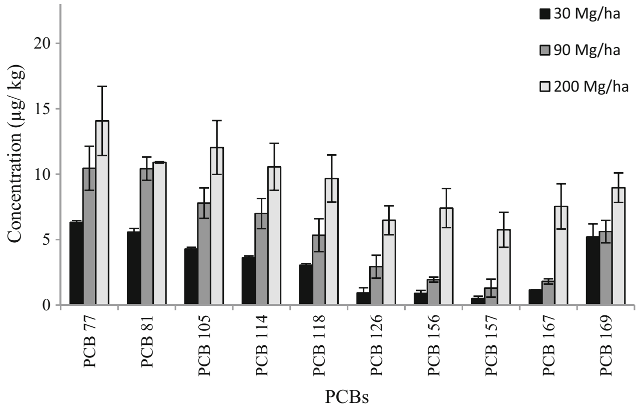


Fig. 3 Concentrations of PCBs in leaching from soil amended with different doses of biosolid after 33 h leaching. Error bars indicate ± SD (*n* = 3)

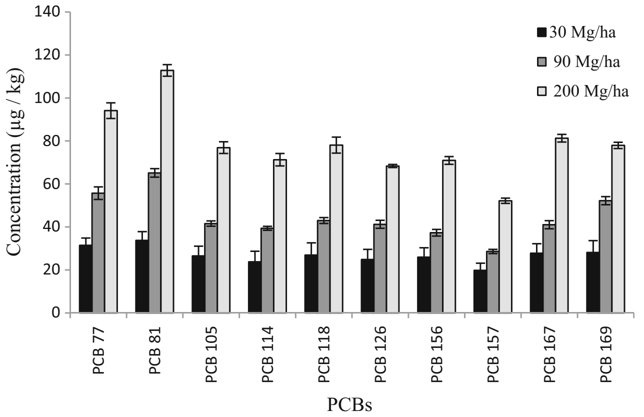


Fig. 5 Concentration of PCBs in roots of wheat plants cultivated by 30 days with different biosolid doses. Error bars indicate ± SD (*n* = 3)

by wheat root were: 0.5, 0.3 y 0.2% for 30, 90 and 200 Mg/ha of biosolid doses respectively. As can be seen in Fig. 6a, b, the bioavailable fraction behaves similarly to the leaching fraction regarding Log K_{ow} and Log S, showing similar determination coefficients. However, despite this, it should be pointed out that the leaching fraction resulted about 20 times higher than the bioavailable fraction, corresponding the former to the

Fig. 4 Correlation between leachable fraction with **a** Log K_{ow} and **b** Log S obtained at different biosolid rates. In dashed black line the ordinary least squares (OLS) fitting

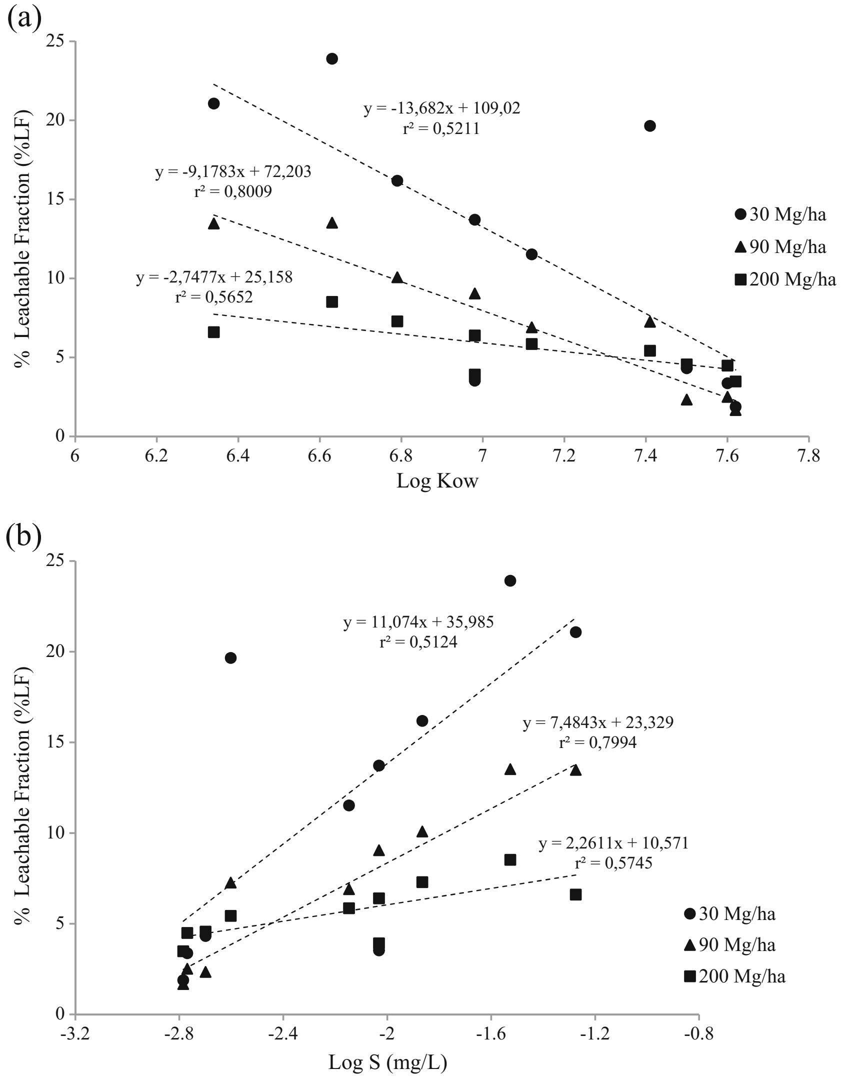
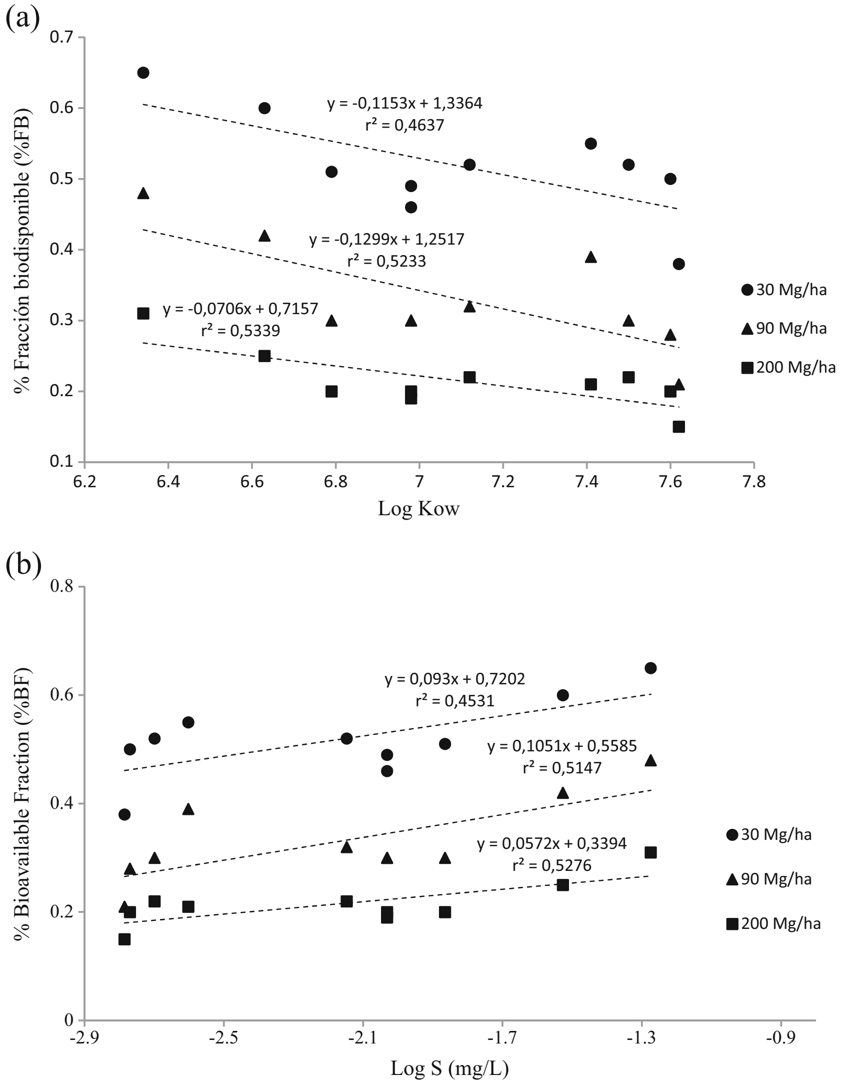


Fig. 6 Correlation between bioavailable fraction with **a** Log K_{ow} and **b** Log S obtained at different biosolid rates. In dashed black line the ordinary least squares (OLS) fitting



bioaccessible fraction instead of the bioavailable one (Wong and Bidleman 2011; Fang et al. 2009; Semple et al. 2007). The high levels found in the leachable fraction, compared to the bioavailable fraction, are a consequence of the addition of methanol to the leaching solution, to prevent PCB sticking to the walls of the vial, which favored the increase of PCB solubility.

The decreasing of the absorbed fraction (bioavailable fraction) by roots is influenced for he hydrophobicity and lipophilicity of the compound (Engwall and Hjelm 2000; Wyrwicka et al. 2014), making them poorly taken up by plants; previous studies also have addressed that part of the original PCBs suffers processes of metabolism in plants (Passatore et al. 2014). being other aspect for the low levels observed in bioavailable fraction compared with the leaching fraction. In Fig. 6a, b the progressive decrease in bioavailability is observed with increasing of biosolid doses, as well as with the degree of chlorination of the molecule that is associated with the Log K_{ow} and Log S.

Relationship between leachable and bioavailable fraction

Both the roots of wheat plants and the PDMS phase (RDSE technique), capture the freely dissolved fraction of the hydrophobic organic compounds (HOC); these HOCs are often complexed with dissolved organic matter (DOM) (Gallé et al., 2005). When biosolid is added to the soil with gradual dose increases, there is also an increase in DOM and the HOC bioconcentration is decreased. This HOC-DOM complex is too large to cross the membranes of living organisms and the case of the PDMS phase; there is a similar situation, because this HOC-DOM complex does not cross the boundary layer of the PDMS; consequently, this analog behavior allows both methods to be correlated with each other. In this context, the leachable fraction (LF) of each PCB under study was correlated with the bioavailable fraction (BF)

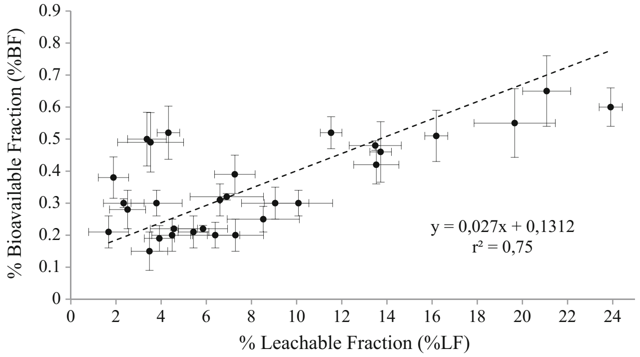


Fig. 7 Correlation between % bioavailable fraction and % leachable fraction of each PCB and biosolid doses under study, in dashed black line the bivariate least squares (BLS) fitting. Error bars indicate ± SD (*n* = 3)

obtained from plant uptake (Fig. 7), applying bivariate least squares regression (BLS), method that considers errors in both axes (Del Río et al. 2001). According to the correlation between both fractions, the coefficients of determination and correlation were $r^2 = 0.75$ and $r = 0.86$, respectively; the biomimetic proposed method allows estimating the bioavailable fraction of PCBs by equation BF = 0.027LF + 0.1312 obtained from model; the BF is about the 2.7% of the LF. The model is valid for PCB congeners considered, according to the conditions established in the experiment and taking into account a global dispersion about to the regression line of 1.84.

A survey of the literature showed that most of the methods used to predict bioavailability of PCBs are mainly related with animal models (Table 5) being still a lack of predictive models related to plant uptake. The main advantage of the proposed method is its rapidity, compared with those used to estimate the bioavailability of PCBs related with plant uptake wherein triolein-embedded cellulose acetate membrane (TECAM) was used (Table 5).

The time involved in the extraction and cleanup are not required in the biomimetic method proposed in this study, which further minimizes operating time.

Conclusions

The fraction of PCB leached from the soil to the aqueous phase depends on both the degree of hydrophobicity of each PCB congener and on the biosolid doses applied to the soil. Given the extreme low polarity of PCBs, their primary interaction is with the hydrophobic organic matter contained in the soil–biosolid mixture. Regression models of the leachable fraction with K_{ow} and water solubility presented better determination coefficients than those obtained with the bioavailable fraction, because the chemical method is not subject to biological variations as in the case of bioassays. Living organisms present heterogeneity in growth, the possibility of biodegradation, and other variables that depend on the organism, which influences the absorption and affinity for different PCBs. Despite this, a good correlation was observed in both fractions ($r = 0.86$). The most important feature of this biomimetic method compared to other reported biomimetic methodologies is that it has the shortest equilibration time (approx. 30 h) and the use of small amounts of sample. In this approach, difficulties associated with variables and in vivo tests are avoided. Future studies would be focused on applying the method to other less persistent hydrophobic compounds having different structural features than PCBs, so to evaluate the leaching behavior and also compare it with bioassays in wheat plant.

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