Concentrations of persistent organic pollutants (POPs) and heavy metals in soil from San Luis Potosí, México

Francisco Javier Perez-Vazquez · Rogelio Flores-Ramirez ·
Angeles Catalina Ochoa-Martinez · Sandra Teresa Orta-Garcia ·
Berenice Hernandez-Castro · Leticia Carrizalez-Yañez · Iván N. Pérez-Maldonado

Abstract The aim of this study was to assess the levels of polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), p,p'-dichlorodiphenyltrichloroethane (DDT), p,p'-dichlorodiphenyldichloroethylene (DDE), and four heavy metals (arsenic, cadmium, lead, and mercury) in soil from the city of San Luis Potosí in Mexico. In order to confirm the presence of the previously mentioned compounds, outdoor surface soil samples were collected and analyzed by gas chromatography/mass spectrometer for PBDEs, PCBs, DDT, and DDE. Meanwhile, heavy metals were quantified using the atomic absorption spectrophotometry technique. The total PBDEs levels ranged from 5.0 to 134 μg/kg dry weight (dw), with a total mean PBDEs level of 22.0±32.5 μg/kg dw (geometric mean± standard deviation). For PCBs, the total mean level in the studied soil was 21.6±24.7 μg/kg dw (range, <LOD to 80.5). An important finding in our study was that all soil samples (100 %) had detectable levels of the metabolite DDE. Moreover, the total mean DDT level (∑ DDT and DDE) was approximately 5.50±4.50 μg/kg dw. The mean levels for arsenic, mercury, cadmium, and lead in soil samples were 7.20±10.7 (range, 15.0 to 265 mg/kg dw), 0.45±0.48 (range, <LOD to 2.50 mg/kg dw), 3.00±3.00 (range, 1.00–13.0 mg/kg dw), and 108±105 (range, 25.0 to 435 mg/kg dw), respectively. This screening study provides us with concentration data for the occurrence of persistent organic pollutants (POPs) and four heavy metals in soil samples from the city of San Luis Potosí, Mexico, and considering that soil is an important pathway of exposure for people, a biomonitoring program for the surveillance of the general population in the city of San Luis Potosi is necessary.

F. J. Perez-Vazquez · R. Flores-Ramirez ·
A. C. Ochoa-Martinez · S. T. Orta-Garcia ·
L. Carrizalez-Yañez · I. N. Pérez-Maldonado
Laboratorio de Toxicología Molecular, Centro de
Investigación Aplicada en Ambiente y Salud (CIAAS),
Coordinación para la Innovación y Aplicación de la Ciencia y
la Tecnología (CIACYT), Universidad Autónoma de San Luis
Potosí,
San Luis Potosí, Mexico

F. J. Perez-Vazquez · R. Flores-Ramirez ·
A. C. Ochoa-Martinez · S. T. Orta-Garcia ·
L. Carrizalez-Yañez · I. N. Pérez-Maldonado
Facultad de Medicina, Universidad Autónoma de San Luis
Potosí,
San Luis Potosí, Mexico

B. Hernandez-Castro
Departamento de Inmunología, Facultad de Medicina,
Universidad Autónoma de San Luis Potosí,
San Luis Potosí, Mexico

I. N. Pérez-Maldonado
Unidad Académica Multidisciplinaria Zona Media,
Universidad Autónoma de San Luis Potosí,
San Luis Potosí, Mexico

I. N. Pérez-Maldonado (✉)
Avenida Sierra Leona No. 550, Colonia Lomas Segunda
Sección, San Luis Potosí 78210 SLP, Mexico
e-mail: ivan.perez@uaslp.mx

Introduction

Contamination caused by metals and persistent organic pollutants (POPs) exists in different areas of Mexico, such as those associated with mining, agriculture, major industry, small-scale industry, oil fields, and non-controlled waste disposal sites (Trejo-Acevedo et al. 2009). Regarding this, a number of studies have previously shown contamination caused by POPs and heavy metals in the soil in those sites in Mexico (Costilla-Salazar et al. 2011; Jasso-Pineda et al. 2007; Martínez-Salinas et al. 2011; Perez-Maldonado et al. 2010; Torres-Dosal et al. 2012). Moreover, exposure studies done in those sites have shown that the populations living in those areas are exposed to POPs and metals (Alegría-Torres et al. 2013; Domínguez-Cortinas et al. 2013; Martinez et al. 2012; Martínez-Salinas et al. 2012; Orta-Garcia et al. 2012; Orta-García et al. 2014; Perez-Maldonado et al. 2010, 2014, 2013, 2014b; Pruneda-Álvarez et al. 2012; Trejo-Acevedo et al. 2012a, b, 2013). However, studies evaluating the concentrations of heavy metals and POPs in environmental and biological samples in urban sites (such as the city of San Luis Potosi) in Mexico are scarce.

These compounds (POPs and heavy metals) are the results of anthropogenic processes and can be introduced into the environments through various routes. In this regard, soil can be a natural sink due to its high affinity for particle bonding with hydrophobic organic pollutants and heavy metals, serving as an important route for these pollutants to enter the environment and the wildlife food chains (Cai et al. 2008; CEPA Canadian Environmental Protection Act 1999; de Wit 2002; She et al. 2004). Moreover, several studies have identified soil as an important pathway of toxicant exposure. Often, the levels of pollutants found in soil including compounds that were banned long ago such as p,p'-dichlorodiphenyltrichloroethane (DDT) are significant sources of exposure for the general population (Butte and Heinzow 2002; Hwang et al. 2008; Rudel et al. 2003).

Recently, three subfamilies of compounds included in the POPs family have gained more interest in Mexico: polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and DDT and its metabolites, and due to their toxic characteristics, these compounds are considered to be hazardous to the environment, biota, and humans. For example, in the past decades, concerns have been raised in regard to PCBs and PBDEs because they have been shown to potentiality cause a number of adverse health effects, including reproductive, immunologic, and neurologic disruptions (Dingemans et al. 2011; Hallgren et al. 2001; Westerink 2014). DDT and its metabolites have been associated with neurological effects (Rocha-Amador et al. 2009), asthma (Sunyer et al. 2006), immunodeficiency (Belles-Isles et al. 2002; Bilrha et al. 2003; Cooper et al. 2004; Dallaire et al. 2004; Dewailly et al. 2000; Vine et al. 2000, 2001), apoptosis (Pérez-Maldonado et al. 2004, 2005, 2006, 2011), and DNA damage in immune cells (Herrera-Portugal et al. 2005; Pérez-Maldonado et al. 2011; Yáñez et al. 2004). Similar to POPs, exposure to heavy metals has also been associated with adverse health effects, including impacts on the nervous, cardiovascular, respiratory, gastrointestinal, hepatic, renal, hematopoietic, immunological, and dermatologic systems (Shribman et al. 2013; Taba 2013; Fujiwara et al. 2012; Zheng et al. 2008).

With the above data and taking into account that an assessment of the levels of POPs and heavy metals in environmental and biological samples has not been performed in the city of San Luis Potosi (SLP), the aim of this study was to assess the levels of PBDEs, PCBs, DDT, p,p'-dichlorodiphenyldichloroethylene (DDE), and of four heavy metals (arsenic, cadmium, lead, and mercury) in the soil within the city of San Luis Potosi in Mexico.

Materials and methods

Location

The city of San Luis Potosi is located in the west-central part of the state of San Luis Potosi, at 22° 09′ 04″ N, 100° 58′ 34″ W. The municipality has an area of 1,443 km^2. The city of San Luis Potosi is the state capital. It has an estimated population of 735,886 inhabitants in the city proper and approximately 1,021,688 inhabitants in the metropolitan area (Soledad de Graciano Sanchez and some other small townships inside the urban area), making it the tenth largest metropolitan area in Mexico.

Sampling locations

The city of San Luis Potosí was divided into four areas depending on their main activity as shown in Table 1 and Fig. 1. In order to confirm the presence of PCBs, PBDEs, DDT, DDE, and the four heavy metals (arsenic, cadmium, lead, and mercury), outdoor surface soil samples (1–5 cm in depth) were collected using a metal blade at the points shown in Fig. 1. The amount of soil collected at each sampling point was approximately 1,000 g. All collected samples were wrapped in aluminum foil and sealed in valve bags stored at −20 °C in the laboratory before being analyzed. A total of 26 samples were collected in all areas tested (Table 1 and Fig. 1).

PBDEs analysis

For PBDEs in soil, we determined the concentrations of five PBDEs congeners (International Union for Pure and Applied Chemistry numbers 47, 99, 100, 153, and 154). Briefly, 1 g of soil was accurately weighed and placed in Green-Chem LEV glasses and was extracted with a mixture of acetone and hexane (1:1). The extraction was performed in a microwave oven (CEM) and allowed to cool at 4 °C in a cold room. The extract was filtered (0.45 μm) and diluted with hexane/dichloromethane (1:1) to 20 mL then evaporated to 4 mL, and hexane/dichloromethane (1:1) was added three times (4 mL). The extract was cleaned with florisil columns (1,000 mg/6 mL, Baker) and then eluted with 20 mL of hexane/dichloromethane (1:1). The elutes were evaporated and dried with a slight warming under

nitrogen gas flow and diluted with hexane to 1 mL. All extraction and cleanup steps were performed in opaque containers, and samples were covered and refrigerated between steps to minimize exposure to light.

We performed a final analytical determination of the target analytes using gas chromatography (GC-HP6890) coupled with a mass spectrometer (MS-HP5973). A DB-5HT column, 15 m × 0.25 mm ID and 0.10-μm film thickness, was used (J&W Scientific, Bellefonte, PA, USA). The column temperatures were as follows: initial, 80 °C (1 min); final, 300 °C (rates of 10 °C/min up to 270 °C and 30.0 °C/min up to 300 °C). The temperature of the injector was 250 °C operated in pulsed splitless mode. Helium was used as the carrier gas at a linear velocity of 1.0 mL/min. The mass spectrometer was operated in selective ion mode (SIM). We used BDE-77 (2 μg/kg) as recovery surrogate standards. Under these conditions and using the data of nine replicates near the lowest concentration attainable at the calibration curve, the method detection limits for all PBDEs assessed were approximately 0.10 μg/kg. An internal control at 2.0, 4.0, and 10.0 μg/kg for all compounds was included in all the analyses series. At these concentrations, the between-assay variation coefficient was 5.0 % (± 3.0 %) and average recovery for all compounds was between 93 and 118 %. As an external quality control, a standard reference material 2585 (National Institute of Standards & Technology) was used. The recovery percentage was 85–105 % for all tested analytes.

DDT, DDE, and PCBs analysis

We also determined the concentrations of DDT, DDE, and 14 PCB congeners (International Union for Pure and Applied Chemistry numbers 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, and 187). Briefly, 1 g of soil was accurately weighed and placed in Green-Chem LEV glasses and 14 mL of dichloromethane was added. The extraction was performed in a microwave oven (CEM) and allowed to cool at 4 °C in a cold room. The extract was filtered (0.45 μm) and diluted with dichloromethane to 20 mL then evaporated to 4 mL, and hexane was added three times (4 mL). The extract was cleaned with florisil columns (1,000 mg/ 6 mL, Baker), and the target compounds were eluted with 12 mL of diethyl-ether/hexane 6 %. The extract was then evaporated with nitrogen gas flow to approximately 0.5 mL and diluted with hexane to 1 mL.

Table 1 Characteristics of sampling locations

Location	Number	Characteristics
A	8	Locations with approximately 50 brick kilns using different materials as a source of fuel; there is also an important metallurgical industry plant established in this location
B	6	Locations within the city of San Luis Potosi with heavy vehicular traffic; the downtown area of the city of San Luis Potosi
C	6	Industrial complex area in the city of San Luis Potosi
D	6	Location where the main economical source of income is the practice of agricultural activity

Fig. 1 Location of San Luis Potosí, México

The quantification was performed using an HP 6890 gas chromatograph coupled with a HP 5973 mass spectrometer. A HP5-MS column, 60 m × 0.25 mm ID and 0.25-μm film thickness, was used (J&W Scientific, Bellefonte, PA, USA). The column temperatures were as follows: initial, 100 °C (2 min); final, 310 °C (rates of 20 °C/min up to 200 °C, 10.0 °C/min up to 245 °C, 4.0 °C/min up to 280 °C, and 30 °C/min up to 310 °C). The temperature of the injector was 270 °C operated in pulsed splitless mode. Helium was used as the carrier gas at a linear velocity of 1.0 mL/min. The mass spectrometer was operated in SIM mode. α-Hexachlorocyclohexane-C13 (2 μg/kg), endrin-C13 (2 μg/kg), and PCB-141-C13 (2 μg/kg) were added as recovery surrogate standards to all samples. Under these conditions and using the data of nine replicates near the lowest concentration attainable on the calibration curve, the method detection limits for DDT, DDE, and all PCBs were approximately 0.30 μg/kg. An internal control at 2.0, 4.0, and 10.0 μg/kg for all compounds was included in all the analyses series. At these concentrations, the between-assay variation coefficient was 3.0 % (± 2.0 %) and the average recovery for all compounds ranged from 95 to 110 %. As an external quality control, the standard reference material 2585 (National Institute of Standards & Technology) was used. The recovery percentage was 90–110 % for all tested analytes.

Heavy metal analysis

The soil samples were oven-dried at 30 °C for 1 to 2 days. Then 1 g of soil was accurately weighed and placed in a 100-mL volumetric flask and 20 mL of HNO_3 25 % were added. The digestion was performed in a microwave oven (CEM) and was allowed to cool off at room temperature. The digest was filtered (0.45 μm) and diluted with deionized water to 20 mL. Lead and cadmium chemical analyses were carried out by flame atomic absorption spectrometry using Varian Spectra AA 220 atomic absorption spectrometer. Arsenic and mercury were analyzed by flame atomic absorption spectrometry using Perkin Elmer 2380 atomic absorption spectrometer coupled to Perkin Elmer MHS-10 hydride generation system (Gamiño-Gutiérrez et al. 2013; Costilla-Salazar et al. 2011). The digestion procedure and quantification for all heavy metals analysis were verified using the certified reference material from the National Institute of Standards and Technology (NIST, mountain soil 2711), with a recovery percentage of 95±5 % for all heavy metals analyzed.

Statistics

To satisfy normality criteria, the levels of all analyzed compounds in soil were logarithm-transformed. Therefore, all of the results are shown as geometric means.

The mean level of the compounds in soil between areas was compared, using one-way analysis of variance (ANOVA), followed by Tukey's test. For all statistical analyses, we used JMP IN 7.0 software (SAS Institute, Inc., Cary, NC, USA). If the concentration of an individual congener (PBDEs, PCBs, DDT, DDE, arsenic, mercury, cadmium, and lead) was less than the method detection limits (LOD), its concentration was assumed to be LOD/2 for statistical analysis.

Results

The mean concentrations of PBDEs congeners in soil samples (mean level of all sampled zones) are shown in Table 2. The total PBDEs levels ranged from 5.00 to 134 µg/kg dry weight (dw), with a total mean PBDEs level of 22.0±32.5 µg/kg dw (geometric mean±standard deviation). The dominant congener in this study was BDE 153 (11.6±18.4 µg/kg dw), followed by BDE 47 (5.85±7.75 µg/kg dw), BDE 99 (2.20±2.30 µg/kg dw), BDE 154 (1.70±3.70 µg/kg dw), and BDE 100 (0.70±0.40 µg/kg dw; Table 2). Moreover, the BDE 153 congener was detected in approximately 95 % of the samples, while the detection rates for BDE 47 (85 %), BDE 100 (50 %), BDE 99 (65 %), and BDE 154 (10 %) were lower than BDE 153. Figure 2 shows the total mean PBDEs level in each sampled location; the highest total mean PBDEs level was found in location B (31.6± 15.3 µg/kg dw). However, although the total mean PBDEs levels in locations A (23.2±13.0 µg/kg dw) and D (19.7±14.6 µg/kg dw) were lower than location B, no significant differences were found among those
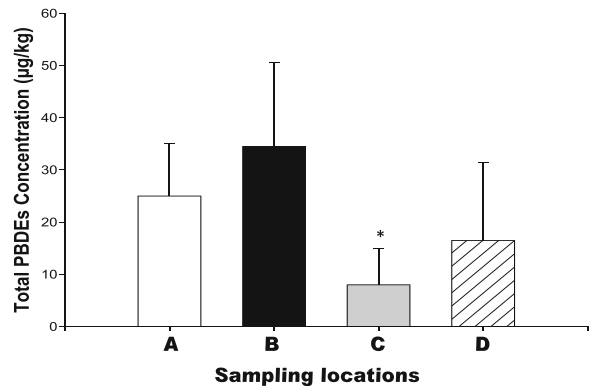
Fig. 2 Total PBDEs concentrations in soil samples of San Luis Potosí, México. Soil concentrations are shown in microgram per kilogram dry weight. Values are geometric means ± standard deviation (SD). *$p<0.05$ when compared to other zones

three locations. But the lowest total mean PBDEs level was found in location C (9.5±5.8 µg/kg dw).

Table 3 shows the levels of PCBs found in soil in the studied sites. The total mean PCBs level was 21.6± 24.7 µg/kg dw (range, <LOD to 80.5 µg/kg). The congeners with the highest concentration in soil were PCB 28 (4.45±3.95 µg/kg dw), PCB 156 (3.00± 2.10 µg/kg dw), PCB 118 (2.65±1.95 µg/kg dw), and PCB 105 (2.20±2.00 µg/kg dw), followed by congeners such as PCB 153 (1.90±2.15 µg/kg dw), PCB 128 (1.60 ±1.95 µg/kg dw), PCB 138 (1.55±2.05 µg/kg dw), PCB 180 (1.10±1.75 µg/kg dw), and PCB 99 (1.05± 1.45 µg/kg dw). The congeners with concentrations under 1.0 µg/kg dw were PCB 52, PCB 101, PCB 170, PCB 183, and PCB 187. In our congener analysis, we assessed three dioxin-like PCB congeners (PCB 105, PCB 118, and PCB 156) and the other nine PCBs

Table 2 PBDEs concentrations in soil from San Luis Potosí, Mexico (µg/kg)

Congener	Mean[a]	SD	PC25	PC50	PC75	PC95	Min	Max
BDE 47	5.85	7.75	0.55	2.60	8.25	22.7	<LOD	27.2
BDE 99	2.20	2.30	0.45	1.70	2.30	7.80	<LOD	8.80
BDE 100	0.70	0.40	0.35	0.50	0.90	1.70	0.20	1.90
BDE 153	11.6*	18.4	1.75	4.55	12.1	21.3	<LOD	81.6
BDE 154	1.70	3.70	0.05	0.05	1.75	11.3	<LOD	14.3
Total PBDEs	22.0	32.5	3.15	9.45	25.3	50.6	5.00	134

Soil concentrations are shown in microgram per kilogram dry weight. The method detection limits (LOD) for all PBDEs were approximately 0.10 µg/kg

SD standard deviation, *PC* percentile, *Min* minimum, *Max* maximum

*$p<0.05$ when compared to other congeners

[a] Values are geometric means

Table 3 PCBs concentrations in soil from San Luis Potosí, Mexico (μg/kg)

Congener	Mean[a]	SD	PC25	PC50	PC75	PC95	Min	Max
PCB 28	4.45*	3.95	4.80	4.85	4.95	11.3	<LOD	21.1
PCB 52	0.70	2.15	<LOD	<LOD	<LOD	6.80	<LOD	10.3
PCB 99	1.10	1.45	<LOD	<LOD	3.15	3.15	<LOD	3.45
PCB 105	2.20*	2.00	<LOD	4.05	4.10	4.10	<LOD	4.30
PCB 118	2.65*	1.95	<LOD	4.10	4.15	4.15	<LOD	4.25
PCB 128	1.60	1.95	<LOD	<LOD	4.05	4.05	<LOD	4.10
PCB 138	1.55	2.05	<LOD	<LOD	4.30	4.30	<LOD	4.75
PCB 153	1.90	2.15	<LOD	<LOD	4.50	4.50	<LOD	4.65
PCB 156	3.00*	2.10	<LOD	4.30	4.35	5.15	<LOD	6.00
PCB 170	0.45	1.10	<LOD	<LOD	<LOD	3.90	<LOD	4.50
PCB 180	1.10	1.75	<LOD	<LOD	<LOD	3.95	<LOD	4.40
PCB 183	0.60	1.30	<LOD	<LOD	<LOD	3.55	<LOD	4.30
PCB 187	0.30	0.80	<LOD	<LOD	<LOD	3.85	<LOD	4.30
Total PCBs	21.6	24.7	4.80	18.7	34.2	62.8	<LOD	80.5

Soil concentrations are shown in microgram per kilogram dry weight. The method detection limits (LOD) for all PCBs were approximately 0.30 μg/kg

SD standard deviation, *PC* percentile, *Min* minimum, *Max* maximum

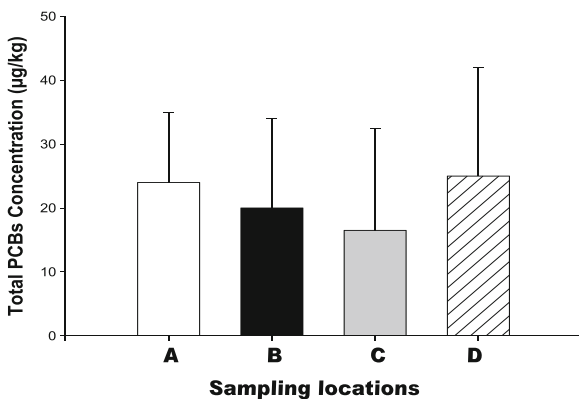*$p < 0.05$ when compared to other congeners

[a] Values are geometric means

analyzed were non-dioxin-like PCB congeners. The total mean level of non-dioxin-like PCB congeners was approximately 13.8 and was 7.8 μg/kg dw for dioxin-like PCB congeners. Figure 3 shows the total mean PCBs level in soil in each of the sampled locations. In contrast with the data found on PBDEs, for PCBs no significant differences were found when total mean PCBs levels were compared among the different

Fig. 3 Total PCBs concentrations in soil samples of San Luis Potosí, México. Soil concentrations are shown in microgram per kilogram dry weight. Values are geometric means ± standard deviation (SD). *$p < 0.05$ when compared to other zones

locations. The total mean PCBs level for location A was 22.5±10.9 μg/kg dw and for location B, 19.1±13.4 μg/kg dw; for soil recollected in location C, the mean level was 16.9±15.1 μg/kg dw; and finally the total concentration of PCBs found in location D was 23.8±17.3 μg/kg dw.

The total mean DDT levels (Σ DDT and DDE) in the studied soil samples (soil samples recollected in four locations) are shown in Table 4. The total mean DDT level in soil was approximately 5.50±4.50 μg/kg dw. Moreover, the mean level for DDT in soil was 0.50± 0.38 μg/kg dw and for DDE it was 5.00±3.90 μg/kg dw (Table 4). An important finding in our study was that all soil samples (100 %) had detectable levels of the metabolite DDE. Finally, Fig. 4 shows the total mean DDT levels in each of the sampled locations; in location A the mean level was 7.20±10.7 μg/kg dw; in location B we found a total mean DDT level of 9.80±7.50 μg/kg dw; in location C, 2.60±3.70 μg/kg dw; and in location D a mean concentration in soil of 5.40±6.20 μg/kg dw was found. No significant differences were found among the total mean DDT levels in the soil from the four assessed locations.

Table 5 shows the mean levels of heavy metals from all analyzed samples. The mean levels for arsenic,

Table 4 DDT and DDE concentrations in soil from San Luis Potosí, Mexico (μg/kg)

Compound	Mean[a]	SD	PC25	PC50	PC75	PC95	Min	Max
DDT	0.50	0.75	<LOD	0.48	3.50	4.50	<LOD	4.90
DDE	5.00*	3.20	<LOD	4.20	12.0	17.40	<LOD	25.6
Total DDT	5.50	5.50	<LOD	6.10	15.5	20.0	<LOD	30.5

Soil concentrations are shown in microgram per kilogram dry weight. The LOD for DDT and DDE were approximately 0.70 μg/kg

SD standard deviation, *PC* percentile, *Min* minimum, *Max* maximum

[a] Values are geometrical means

*$p<0.05$ when compared to DDT

mercury, cadmium, and lead in soil were 7.20±10.7 (range, 15.0 to 265), 0.45±0.48 (range <LOD to 2.50), 3.00±3.00 (range 1.00 to 13.0), and 108±105 mg/kg dw (range 25.0 to 435 mg/kg dw), respectively. The mean levels of heavy metals in each sampled location are shown on Table 6. The highest levels of arsenic were found in location A (69.0±102.0 mg/kg dw) and location C (68.0±92.0 mg/kg dw), compared to the levels found in location B (21.0±3.0 mg/kg dw) and location D (28.0±19.0 mg/kg dw). Regarding mercury, the highest levels were found in location B (0.75±1.0 mg/kg dw) and location C (0.52±0.37 mg/kg dw) and the lowest levels in location A (0.34±0.25 mg/kg dw) and location D (0.24±0.16 mg/kg dw). For cadmium, similar levels in soil from all sampled locations were found, and the mean cadmium levels were 2.0±1.0, 4.0±5.0, 4.0±4.0, and 3.0±2.0 mg/kg dw, in locations A, B, C, and D, respectively. Finally, the mean levels of lead in soil were 45.0±17.0 mg/kg dw in location D (the lowest level of all assessed locations) and 91.0±81.0 mg/kg dw

in location A, 117.0±96.0 mg/kg dw in location B, and 188.0±155.0 mg/kg dw in location C. In conclusion, location C has the soil with the highest concentrations of heavy metals. In contrast, location D is the region in San Luis Potosí with the lowest concentrations of heavy metals assessed.

Discussion

Environmental contamination caused by POPs and heavy metals coupled with the rapid industrialization and urbanization is a serious and worldwide problem in many countries (Tsai 2010). In this regard, soils are not only basic components of our environment as they provide nutrients for living organisms but also serve as reservoirs for deleterious chemical species which cause negative effects on the environment and human health (UNEP 2011).

PBDEs are a group of POPs that have triggered an increasing research interest in recent years due to their possible detrimental effects on human beings and wildlife and for their environmental ubiquity (Costa et al. 2008; Darnerud 2003; Wu et al. 2007). PBDEs were widely used (and in some cases continue to be used) as flame retardants in products, such as plastics, textiles, and electronic circuitry. However, there have been relatively few studies done on the concentrations of PBDEs in soils in South and Central America; as for Mexico, the information is even scarcer. In this context, to our knowledge, this is the first study done in Mexico that assessed PBDEs levels in soils. The total mean PBDEs levels in the soil from San Luis Potosí found in this study was approximately 22.0 μg/kg dw, and a comparison of the PBDEs concentrations between this study and previous studies was conducted. This mean level is
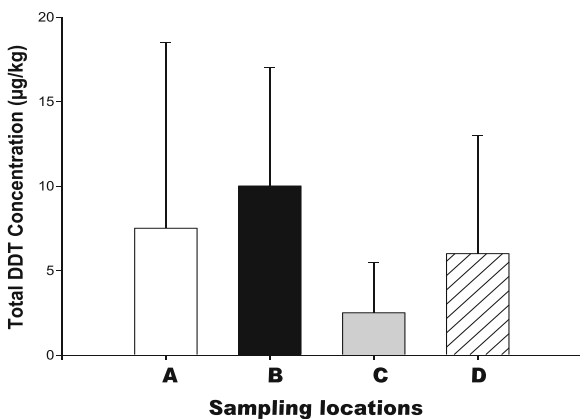
Fig. 4 Total DDT concentrations in soil samples of San Luis Potosí, México. Soil concentrations are shown in μg/kg dw. Values are geometric means ± standard deviation (SD). *$p<0.05$ when compared to other zones

Table 5 Heavy metal concentrations in soil from San Luis Potosí, Mexico (mg/kg)

Compound	Mean[a]	SD	PC25	PC50	PC75	PC95	Min	Max
Arsenic	51.0	76.0	25.0	50.0	75.0	159	15.0	262
Mercury	0.45	0.48	0.18	0.31	0.53	1.70	<LOD	2.34
Cadmium	3.00	3.00	1.90	2.00	3.00	11.6	1.00	12.9
Lead	108	105	38.0	54.3	162	258	25.0	433

Soil concentrations are shown in milligram per kilogram dry weight. The LOD for arsenic, mercury, cadmium, and lead were approximately 0.10 mg/kg

SD standard deviation, *PC* percentile, *Min* minimum, *Max* maximum

[a] Values are geometric means

lower than the reported levels from e-waste sites around the world (Dong et al. 2013; Lopez et al. 2011; Liu et al. 2013). For example, in a study performed in Taizhou, China, which is one of the largest Electrical Waste and Electronic Equipment dismantling areas in the world, concentrations of total PBDEs ranged from 2.96 to 200 μg/kg dw, with a mean of 65.2 μg/kg dw, were found (Dong et al. 2013). However, compared to the PBDEs levels in soil from other countries (no e-waste sites), the total PBDEs concentration in this study was higher (Hassanin et al. 2004; Wang et al. 2009; Parolini et al. 2013; Schuster et al. 2011; Yun et al. 2008; de Wit

Table 6 Heavy metal concentrations in soil from San Luis Potosí, Mexico classified by sampling locations (mg/kg)

Area/Compound	Mean[a]	SE	PC25	PC50	PC75	PC95	Min	Max
A								
Arsenic	69.0*	102	16.0	68.0	129	195	15.0	265
Mercury	0.34	0.25	0.18	0.23	0.43	0.83	0.14	0.92
Cadmium	2.00	1.00	1.95	2.00	3.00	4.80	1.60	5.20
Lead	91.0	81.0	40.0	63.0	119.0	259	37.0	287
B								
Arsenic	21.0	3.00	18.0	21.0	24.0	32.0	5.00	34.0
Mercury	0.75**	1.00	0.22	0.35	0.84	2.20	<LOD	2.40
Cadmium	4.00	5.00	1.80	1.90	9.00	12.5	1.00	13.0
Lead	117	96.0	30.0	114	209	215	25.0	220
C								
Arsenic	68.0*	92.0	16.0	22.0	128	225	15.0	250
Mercury	0.52**	0.37	0.24	0.54	0.75	0.95	<LOD	1.00
Cadmium	4.00	4.00	1.00	2.00	9.00	12.0	1.00	13.0
Lead	188	155	37.0	171	321.0	428	30.0	435
D								
Arsenic	28.0	19.0	19.0	20.0	35.0	58.5	15.0	67.0
Mercury	0.24	0.16	0.13	0.22	0.38	0.48	<LOD	0.50
Cadmium	3.00	2.00	2.00	3.00	4.00	6.50	1.50	7.00
Lead	45.0***	17.0	31.0	42.0	60.0	73.5	25.0	75.0

Soil concentrations are shown in mg/kg dw. The LOD for arsenic, mercury, cadmium, and lead were approximately 0.10 mg/kg

SD standard deviation, *PC* percentile, *Min* minimum, *Max* maximum

*$p < 0.05$ when compared to arsenic levels in locations A and C with other locations; **$p < 0.05$ when compared mercury levels in locations B and C with other locations; ***$p < 0.05$ when compared lead levels in location D with other locations

[a] Values are geometric means

et al. 2010; Zhang et al. 2013; Miglioranza et al. 2013). For instance, in a study performed on urban soil in the UK and Norway, a total PBDEs level of 0.59 µg/kg dw was found in the urban soil samples recollected in 2008 (Schuster et al. 2011).

On the other hand, an important finding in our study was that BDE 153 (detected in 95 % of the assessed samples) was the dominant congener. In contrast, previous studies showed that the concentration of BDE 47 was much higher than that of BDE 153 in North America (Yun et al. 2008). In the past, the largest market for penta-BDE technical mixture was North America, which accounted for approximately 95 % of its sale in 2001 (Birnbaum and Staskal 2004). It is likely that BDE 47 was the most dominant congener in North American soil because it was a major component of the penta-BDE technical mixture (La Guardia et al. 2006). The findings in our study are maybe related to the changes in the environmental accumulation pattern over time but could also be affected by temporal changes. However, there is no definite explanation for this change in the accumulation profile of PBDEs. Another possibility could be the metabolism of BDE 209, leading to the formation of BDE 153 and BDE 154, or the higher persistence of BDE 153 and BDE 154 than that of lower brominated congeners such as BDE 47. These results may indicate that the sources of lower-brominated diphenyl ethers are decreasing. Similar results that were shown in that study were found in a research project performed in soil samples recollected in the north west of the New Territories in Hong Kong (Man et al. 2011) in an open burning site. In Man et al. (2011) study, BDE 47, BDE 99, and BDE 153 were analyzed in soil samples. BDE 153 showed the highest concentration among the congeners in sampled soil, followed by BDE 47 and finally BDE 99. In this regard, it has been demonstrated that the thermal debromination of PBDEs is also possible. In this context, the debromination of PBDEs was well documented elsewhere. For example, Nose et al. (2007) reported that BDE 209 could decompose to more than 99 % at 300 °C during a hydrothermal treatment, and Bezares-Cruz et al. (2004) reported that BDE 209 could debrominate through BDE 207 and BDE 206 step by step to lower-brominated BDE congeners and finally into BDE 99 and BDE 47 in a state of solar photodecomposition. These debromination reactions result in the elevation at different percentages of various debrominated BDE congeners in the emitting pattern compared to commercial PBDE patterns.

Therefore, more studies are necessary in order to assess the true sources of these congeners in San Luis Potosí, Mexico.

The highest concentrations of total PBDEs were found in location B (the urban location), location A (location with brick kilns), and location D (agricultural area). The high PBDE concentration in the urban location (location B) would appear to derive from the intensive use of electrical appliances and home and office furniture at this site. For location A, the main source of contamination is possibly the brick kilns ovens that use several materials (tires, wood, oil, electronic equipment, textile, among others) as energy source. On the other hand, in the agricultural location (D), the soil samples were recollected near the main urban water systems (drainage) in San Luis Potosí, which flow through substantial urban and industrial areas. Moreover, a significant proportion of the land in that area is regularly flooded by the urban water systems. Therefore, the high PBDEs contamination in that location (location D) would be due to the flooded phenomena. Finally, it was found that the total mean PBDEs levels in location C were lower when compared with the other three locations. However, the concentrations at the industrial site (location C) are higher or comparable to those found in soil samples from industrial regions around the world (Parolini et al. 2013; Li et al. 2008, 2009; Romano et al. 2013).

PCBs were once used extensively in the industry, particularly as heat transfer chemicals in electric transformers and capacitors as well as hydraulic fluids and lubricants in heavy electrical equipment (ATSDR 2000). This study showed that the total mean PCBs levels found in the analyzed soil samples recollected in the city of San Luis Potosi were 21.6 µg/kg dw. The guidelines in Mexico for total PCBs are the following: in agricultural soil 0.50 mg/kg, in residential soil 5.00 mg/kg, and in industrial soil 25.0 mg/kg (NOM-133-ECOL-2000). We can note that the total mean PCBs level in San Luis Potosí (Table 3) is lower than the levels in the guidelines in Mexico. Moreover, all sampled locations (A, B, C, and D) have soil levels with total PCBs below the guidelines in Mexico for total PCBs in soil (Fig. 3). When the total mean PCBs level found in our study was compared with the levels found in other locations worldwide, the levels of PCBs in the present study were generally higher than those found in other studies including urban, rural, industrial, agricultural, e-waste areas, and municipal dump site soils

(Batterman et al. 2009; Li et al. 2010; Ilyas et al. 2011). For example, in a study performed by Ilyas et al. (2011) who assessed PCBs contamination in the surface soils from Surabaya, Indonesia at various locations such as industrial, urban, rural, dumping site, and agricultural areas, the levels of these contaminants were observed in decreasing order: industrial district (9.60 μg/kg dw), urban (4.70 μg/kg dw), dumping site (4.10 μg/kg dw), rural (2.80 μg/kg dw), and agricultural areas (0.085 μg/kg dw). However, the levels found in the surface soil of San Luis Potosí were lower than the levels found in surface soil by our work group in San Felipe Nuevo Mercurio, Mazapil, Mexico (total mean PCBs level in soil of approximately 36.0 μg/kg dw). San Felipe Nuevo Mercurio was a mining site in the central region of Mexico. Several years ago, the mine was an area formerly used to store wastes and several hazardous substances, including hundreds of storage drums containing PCBs (Costilla-Salazar et al. 2011). Moreover, when the levels in this study were compared with the levels found in Alpuyeca, Morelos, Mexico (mean total PCBs level in soil of approximately 20,000.0 μg/kg dw; Pérez-Maldonado et al. 2014a), the difference was excessive for the levels found in soil assessed in our study, since the soil had total PCBs levels approximately 1,000 times lower than soil evaluated in Alpuyeca, Morelos (Pérez-Maldonado et al. 2014a). In Alpuyeca, an electric capacitor manufacturing industry was established approximately 45 years ago, where PCBs were used for the fabrication of capacitors. When the industry closed, the empty space was used to store waste containing PCBs (Castro et al. 2008). On the other hand, it has been demonstrated that the toxic effects of PCB congeners are structure-dependent. In this regard, PCB congeners (dioxin-like PCBs) with a coplanar structure are able to bind and activate the aryl hydrocarbon receptor (AhR) and initiate toxic effects similar to those of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, a chlorinated polyaromatic hydrocarbon known to bind to the AhR (Consonni et al. 2012; Aluru et al. 2011). In contrast, existing PCB congeners (non-dioxin-like PCBs) with chlorine substitution at the ortho-positions of the biphenyl rings (non-coplanar congeners) and those congeners are not capable of binding with high affinity to the AhR. However, non-dioxin-like PCBs are also involved in generating toxic effects such as neurotoxicity, endocrine disruption, and immunosuppression (ATSDR 2000; Helmfrid et al. 2012). In this context, non-dioxin-like PCBs are known to be less toxic than dioxin-like PCBs. However, non-

dioxin-like PCBs are most commonly found in environmental matrices and in the blood and tissues of humans and at much higher concentrations than the dioxin-like PCBs (Ferrante et al. 2010, 2011). The results obtained in our work are concordant with the abovementioned studies. The total mean levels of non-dioxin-like PCBs in soil samples (13.8 μg/kg dw) were higher than the total mean levels of dioxin-like PCBs (7.8 μg/kg dw). Finally, when the mean levels of total PCBs between locations were compared, no significant differences were found. This result shows the wide distribution of PCBs, and we can assume that a major part of the total PCBs levels found in the soil of San Luis Potosí come from medium long-range atmospheric transport. However, other local sources such as waste and electronic-waste dumping sites cannot be excluded.

DDT was the most widely used organochlorine pesticide in the world. It is considered a pollutant of high persistence due to its half-life of up to 15 years in the environment (ATSDR 2002; Turusov et al. 2002). The total DDT levels found in this study were lower than the levels found in some parts around the world (Song et al. 2012; Maliszewska-Kordybach et al. 2013; Ge et al. 2013; Mishra et al. 2012; Perez-Maldonado et al. 2010). For example, when the levels found in our study were compared with levels found in Mesoamerican countries (Perez-Maldonado et al. 2010), it was noted that the levels of total DDT in soil were lower (mean total DDT levels of 180 μg/kg dw; Perez-Maldonado et al. 2010). Moreover, when we compared our results (this study) with the levels in soil found in other parts of Mexico (Martínez-Salinas et al. 2011; Torres-Dosal et al. 2012; Perez-Maldonado et al. 2010; Martinez et al. 2012), the difference was excessive for the soil assessed in our study. For example, in Chiapas in the Southeastern Region of Mexico, the levels in soil found by Martínez-Salinas et al. (2011) ranged from 2 to 27,000 μg/kg dw. Similar to Chiapas, the levels in Chihuahua (range, 1 to 16,500 μg/kg dw) which is in the Northern Region of Mexico (Martinez et al. 2012) are higher than the levels found in this study. It is important to mention that the communities assessed in southeastern and northern regions of México were sprayed with technical DDT several years ago as part of the health campaigns for the control of malaria. Finally, when the total mean levels of DDT between locations were compared, no significant differences were found. It is important to remember that DDT in Mexico was used mainly for health campaigns (in

malaria-endemic communities). The city of San Luis Potosí is not a malaria-endemic region and therefore, very few amounts of DDT were used in the past in that location. Therefore, similar to PCBs, we can assume that a major part of the total DDT levels found in the soil from San Luis Potosí come from medium long-range atmospheric transport.

On the other hand, the guidelines for arsenic, lead, cadmium, and mercury in Mexico in agricultural/residential soil are 25, 400, 35, and 25 mg/kg, respectively, and for industrial soil are 260, 800, 450, and 310 mg/kg, respectively (NOM-147-SEMARNAT/SSA1-2004). It is important to mention that this guideline is for the remediation of soil in agricultural/residential and industrial zones. The mean arsenic level found for all the analyzed soil samples in San Luis Potosí City was 51.0 mg/kg, which surpassed the Mexican guideline for agricultural/residential soil. When we compared the levels found in each examined location, we note that locations A (area with an important metallurgy industry plant in México), C (industrial complex area), and D (agricultural location) have higher levels than the ones in the guideline for agricultural/residential soil. However, no locations with higher levels than the ones in the industrial guideline in soil for Mexico were found in this study. For lead, cadmium, and mercury, the mean levels found in all analyzed soil samples were lower than the values given by the Mexican guidelines for agricultural/residential and industrial zones. Similar results were found when the levels in each tested location (A, B, C, and D) were compared to the Mexican guidelines (Table 6); all locations had levels in soil for three heavy metals (lead, cadmium, and mercury) lower than guidelines in México for agricultural/residential and industrial locations. However, when compared to the Canadian guidelines for the protection of environmental and human health (Environment Canada 1999), the soil in San Luis Potosí, Mexico had higher levels for arsenic, lead, and cadmium (Table 5) than the Canadian guidelines for agricultural soil (12, 70, and 1.4 mg/kg for arsenic, lead, and cadmium, respectively). Moreover, the arsenic levels in soil of all tested locations (Table 6) were higher than Canadian guidelines for agricultural (12.0 mg/kg), residential (12.0 mg/kg), and industrial (12.0 mg/kg) soil. Similar results as the ones for arsenic were found for cadmium in soil (all locations had cadmium levels in soil higher than the Canadian guideline for agricultural soil). However, tested locations (A, B, C, and D) had levels lower than Canadian guidelines for

residential (10 mg/kg) and industrial (22 mg/kg) soil. As for lead, we note that locations A, B, and C had levels in soil higher than the Canadian guideline for agricultural soil (70 mg/kg), and only location C had levels in soil higher than residential guidelines for Canada (140 mg/kg) in which the guideline for industrial soil for lead is 740 mg/kg. The levels found in soils in this study were lower than the levels found in hot spot sites in México for heavy metals, such as mining sites (Gamiño-Gutiérrez et al. 2013), smelter sites (Carrizales et al. 2006), and abandoned mining locations (Naranjo-Pulido et al. 2002; Ongley et al. 2007). Moreover, when comparing the heavy metal levels in soil found in this study to the levels found in hot spot sites for those compounds (heavy metals) around the world, such as e-waste recycling sites (Quan et al. 2014; Zhang et al. 2014), mining sites (Agnieszka et al. 2014), and industrial sites (Xu et al. 2014), the levels found in soil samples from San Luis Potosí were lower.

It is important to remember that comparisons of heavy metal and POPs concentrations across regions or countries are not straightforward as several factors can be important determinants in soil concentrations and must be taken into account. These include timely aspects, such as time of soil collection, technical considerations, the specific congeners measured, and physicochemical properties of soil samples.

Finally, our study has several limitations, the most notable of which is the small sample size; also a human and ecological risk characterization is necessary in order to understand the real significance of our results. However, the moderately high POPs and metal levels found in soil samples from the city of San Luis Potosí highlight the necessity of completing a survey on the background concentration of those compounds in soil; considering that soil is an important pathway of exposure for people (Butte and Heinzow 2002; Hwang et al. 2008; Rudel et al. 2003), a biomonitoring program for the surveillance of the general population in the city of San Luis Potosi is necessary. In this context, humans and all other organisms are typically exposed to multi-component chemical mixtures, present in the surrounding environmental media (water, air, and soil), in food, or in consumer products. However, with a few exceptions, chemical risk assessment considers the effects of single substances in isolation, an approach that is only justified if the exposure to mixtures does not bear the risk of an increased toxicity. This would be the case, for instance, if only one chemical of the mixture is toxic and the

others are biologically inert, or if empirical evidence showed that the joint action of chemicals is typically not larger than the effect of the most toxic compound. Thus, a health risk assessment of simultaneous exposure to organic and inorganic pollutants in the studied area is necessary.

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