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Original Research

Human Health Risk Assessment of Organophosphate Esters in Urban Topsoils of Shenyang, China

Qing Luo*, Leiyan Gu, Yue Shan, Hui Wang, Lina Sun

Key Laboratory of Regional Environment and Eco-Remediation of the Ministry of Education,
College of the Environment, Shenyang University, Shenyang, China

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Abstract

The human health risk of organophosphate esters (OPEs) in the urban topsoils of Shenyang, China was assessed in this study. Seventy-four topsoil samples were collected and analyzed, and ∑OPE concentrations varied from 0.0387 to 0.9522 mg/kg -dry weight (dw). OPE concentrations in east and west Shenyang are high, but in the north and south are low. Compared with other studies, OPE pollution levels are higher than farmland soils and lower than site soils, but are similar to other urban soils. The carcinogenic risks ranged from 2.30×10^{-11} to 4.16×10^{-10} and 2.21×10^{-11} to 4.00×10^{-10} for adults and children respectively. The non-carcinogenic risks ranged from 1.61×10^{-6} to 2.84×10^{-5} and 6.17×10^{-6} to 1.09×10^{-4} for adults and children, respectively – well below acceptable levels. Tris-(2-chloroethyl) phosphate (TCEP) is the most important carcinogen, tris-(1-chloro-2-propyl) phosphate (TCPP), 2-ethylhexyl diphenyl phosphate (EHDPP) and tri-iso-butyl phosphate (TiBP) are the most important non-carcinogens. OPE concentrations are the most sensitive parameter that contributed the largest to the total variance of risk, TCEP is the most influential variable for carcinogenic risk, and TCPP, EHDPP and TiBP are the most influential variables for non-carcinogenic risk.

Keywords: organophosphate esters, spatial distribution, carcinogenic risk, non-carcinogenic risks, sensitivity analysis

Introduction

Organophosphate esters (OPEs) are a class of synthetic chemical additives that as the primary substitute of polybrominated diphenyl ethers (PBDEs) have been extensively used as flame retardants and plasticizers in various commercial products [1]. Due to OPEs not bonding chemically to the finished products, they are easy to release into the surrounding environment through abrasion, volatilization and leaching. In recent years, OPEs have been ubiquitously found in all kinds of environmental media (water, sediment, soil, etc.) and living organisms [1-3], plus in blood, breast milk and placenta for different concentration levels [4].

However, OPEs are not safe and are potentially harmful to the ecosystem and humans. Thus far, most OPEs have been proven to induce toxicity effects on

*e-mail: luoqingyt@126.com

neurological, reproductive, endocrine and immune systems [5]. For example, triphenyl phosphate (TPhP) or cresyl diphenyl phosphate (CDP) can impede the cardiac looping progress of zebrafish embryos [6] while tris (1,3-dichloro-2-propyl) phosphate (TDCP) has adverse effects on the reproduction of zebrafish [7]. In particular, it should be noted that these toxic effects occurred in the environmental concentrations.

In view of the serious toxic effects of OPEs and their wide distribution in the environment, their environmental exposure and health risk assessment should be carried out. At present, research about the exposure and risk assessment of OPEs are concentrated in the air, dust and water [8, 9]. However, most of this research is preliminary due to not dividing the risk of OPEs into carcinogenesis and non-carcinogenesis, or only considering one exposure pathway. Many pollutants, including OPEs, will eventually converge to soil and endanger human health through ingestion, dermal contact, and inhalation, so the exposure and risk assessment of pollutants in soil is important [10-13]. However, research about exposure and risk assessment of OPEs in soil is limited.

Therefore, Shenyang, a typical and famous heavy industry city in China, was selected as the study area in the present study. We assessed the exposure and health risk of OPEs in topsoil from the central area of Shenyang. The results of this study will be beneficial to the risk assessment and remediation benchmark of OPEs in urban soil.

Materials and Methods

Study Region and Soil Sampling

The central area (within the Third Ring Road) of Shenyang, China was selected as the study region (Fig. 1). Shenyang, the largest city in northeast China, has a heavy industrial base dominated by the equipment manufacturing industry. Construction and agricultural by-products processing, chemical products manufacturing, steel and non-ferrous metal smelting are also important industries. The urban area is 3495 km^2, and the residential population exceeds 8 million. Using the uniform grid method, 74 topsoil samples (0-10 cm depth) were collected in September 2017. The sampling sites are shown in Fig. 1. In each sample site, we collected 5 samples and mixed them together as one sample. After collection, the samples were transported to our lab in an ice bath. Then the soil samples were freeze-dried, ground and sieved (1 mm mesh). The fraction below 1 mm was collected and stored at -20ºC before extraction.

Sample Analysis

Thirteen OPEs, including triethyl phosphate (TEP), tripropyl phosphate (TPrP), tri-iso-butyl phosphate (TiBP), tributyl phosphate (TnBP), tris-(2-chloroethyl) phosphate (TCEP), tris-(1-chloro-2-propyl) phosphate (TCPP), TDCP, tri-butoxyethyl phosphate (TBEP), TPhP, 2-ethylhexyl diphenyl phosphate (EHDPP),

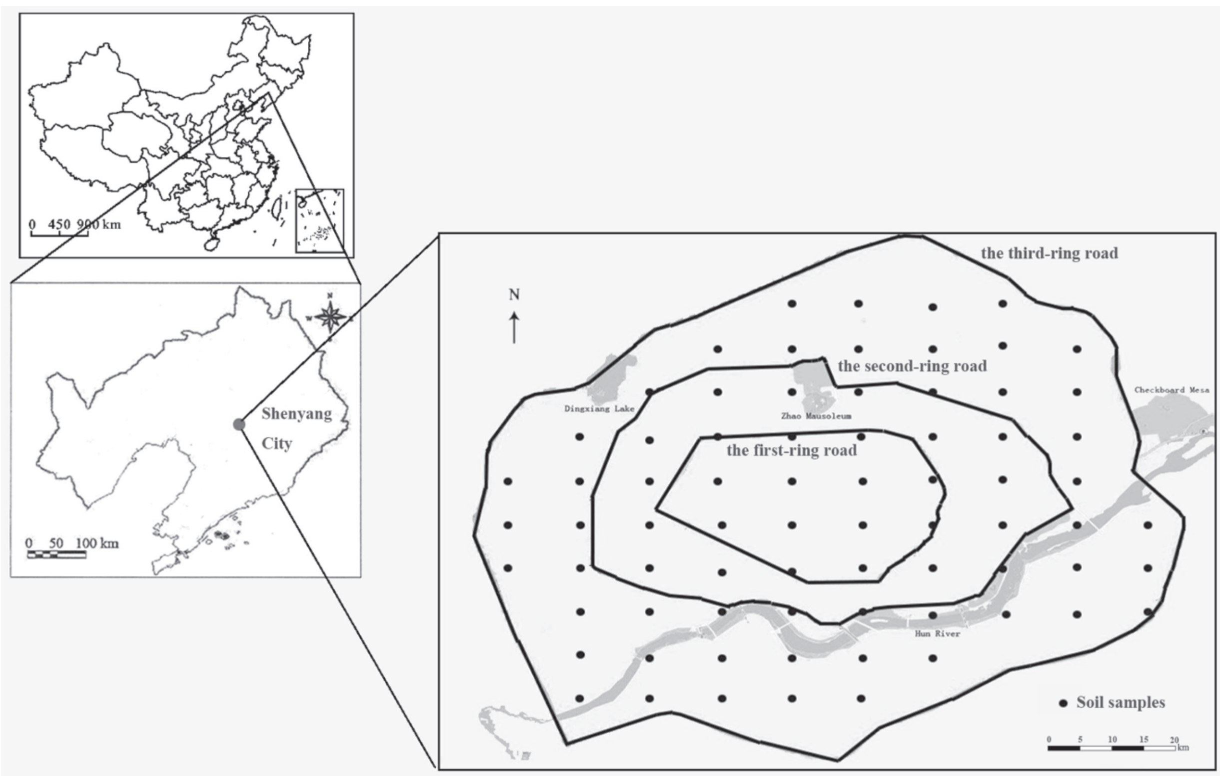

Fig. 1. Distribution of sampling sites in Shenyang, China.

tri(2-ethylhexyl) phosphate (TEHP), triphenylphosphine oxide (TPPO) and tricresyl phosphates (TCrPs) were analyzed in this study. The OPEs in soil samples were extracted and analyzed by our previous method [14]. Briefly, an accurately weighed 10 g soil sample was spiked with 20 ng TnBP-d_{27} and TPhP-d_{15} as internal standards, and the mixture was then loaded into a 34 mL stainless steel extraction cell preloaded with 5 g silica gel and 2 g copper powder as the purification materials. After that, the samples were exacted by accelerated solvent extraction (ASE, Dionex, Sunnyvale, CA, USA). The ASE operating conditions were: extraction solvent was *n*-hexane:acetone (1:1, v:v), extraction temperature was 100ºC, extraction pressure was 1500 psi, static extraction time was 10 min, flush volume was 60%, nitrogen purge time was 60 s and the number of extraction cycles was 2. The extracts were evaporated and blown down to dryness, then the residues were redissolved with 100 μL of hexane. The samples were then analyzed by Thermo Trace GC Ultra coupled with a Thermo fisher PolarisQ ion trap mass spectrometer (Thermo fisher, USA). The GC column was the TR-5MS capillary column (30 m × 0.25 μm × 0.25 mm). The carrier gas was helium and the flow rate was 1 mL/min. The oven temperature program was 50ºC for 1 min, 10ºC/min to 180ºC and hold for 8 min, 20ºC/min to 240ºC and hold for 8 min, 3ºC/min to 255ºC, 30ºC/min to 300ºC and kept at that temperature for 5 min. The sample was injected in the splitless mode with a pulse pressure of 20 psi for 1 min and the injected volume was 2 μL. The temperatures of injection port, interface and ion source were set at 250, 280 and 250ºC, respectively. The MS detection was in multiple reaction monitoring (MRM) mode at an electron impact energy of 70 eV.

Quality assurance and quality control (QA/QC) was conducted by reagent blanks, duplicates, and spiked samples. The recoveries ranged from 81.7 to 107%. Three duplicates were used for all the samples, and the relative standard deviations of duplicate samples were less than 12%. The method detection limit (MDL) ranged from 0.0001 mg/kg -dry weight (dw) for TnBP to 0.00022 mg/kg -dw for TCEP, and the method quantitation limit (MQL) ranged from 0.00033 mg/kg -dw for TnBP to 0.00072 mg/kg -dw for TCEP and TCrPs.

Health Risk Assessment

Health risk assessment is used to evaluate the harm degree of environmental pollutants to human health. According to the toxicity, the risks of pollutants are divided into non-carcinogenic and carcinogenic. The non-carcinogenic and carcinogenic risks were quantitatively described by hazard quotient (HQ) and cancer risk (CR), respectively [15].

For the topsoil, the pollutants can affect human health dominated by three exposure pathways, including ingestion, dermal contact and inhalation. In order to assess the exposure level received by a human, the chronic daily intake (CDI) via these three pathways was calculated by the following equations:

$$CDI_{ingestion} = \frac{C_{soil} \times IR \times CF \times ED \times EF}{BW \times AT} \quad (1)$$

$$CDI_{dermal\ contact} = \frac{C_{soil} \times CF \times SA \times AF \times ABS \times ED \times EF}{BW \times AT} \quad (2)$$

$$CDI_{inhalation} = \frac{C_{soil} \times HR \times ED \times EF}{PEF \times BW \times AT} \quad (3)$$

…where $CDI_{ingestion}$, $CDI_{dermal\ contact}$, and $CDI_{inhalation}$ are the chronic daily intake from ingestion, dermal contact and inhalation, respectively, mg/kg-day;

Table 1. Relative parameters used in human health risk assessment.

Parameters	Unit	Exposure subjects		References
		Children	Adults	
IR	mg/day	50	20	[15, 16, 17]
EF	day/year	350	350	[18]
ED	year	6	24	[15, 16, 19]
BW	kg	29	63	[16, 20]
AT	day	2190 (non-carcinogenic) 25550 (carcinogenic)	8760 (non-carcinogenic) 25550 (carcinogenic)	[15]
HR	m^3/day	7.6	16	[20]
PEF	m^3/kg	1.4×10^9	1.4×10^9	[21]
SA	cm^2	2800	5700	[22]
AF	mg/cm^2	0.2	0.07	[15]
ABS	unitless	0.1	0.1	[21]
GIABS	unitless	1	1	[21]

C_{soil} is the concentration of OPE in soils, mg/kg; IR is the ingestion rate, mg/day; EF is the exposure frequency, day/year; ED is the exposure duration, year; BW is the body weight of the exposed individual, kg; AT is the average time, day; HR is the air inhalation rate, m^3/day; PEF is the particle emission factor, m^3/kg; SA is the surface area of exposed skin, cm^2; AF is the relative skin adherence factor, mg/cm^2; ABS is the dermal absorption factor, unitless; and CF is the conversion factor, equal to 10^{-6} kg/mg. The parameter values are given in Table 1, which are different for children (aged 1-17) and adults (aged 18-).

For non-carcinogenic risk, the HQ is equal to the CDI divided by the corresponding reference dose (RfD). Due to the lack of evidence for the interactive effects of OPEs, the total hazard index (THI) is calculated by summing the HQ of all OPEs.

$$\mathrm{HQ} = \mathrm{HQ_{ingestion}} + \mathrm{HQ_{dermal\ contact}} + \mathrm{HQ_{inhalation}} = \frac{\mathrm{CDI_{ingestion}}}{\mathrm{RfD}} + \frac{\mathrm{CDI_{dermal\ contact}}}{\mathrm{RfD \times GIABS}} + \frac{\mathrm{CDI_{inhalation}}}{\mathrm{RfC}} \quad (4)$$

$$\mathrm{THI} = \sum \mathrm{HQ_x} \quad (5)$$

…where RfD is the corresponding oral reference dose, mg/kg-day; GIABS is the gastrointestinal absorption factor, unitless; RfC is the corresponding inhalation reference concentration, mg/m^3; and x indicates the number of pollutants.

For carcinogenic risk, the CR is determined by multiplying CDI by the corresponding cancer slope factor (SF) of each exposure pathway. Due to the same reasons, the total cancer risk (TCR) is defined by adding the CR of each OPE.

$$\mathrm{CR} = \mathrm{CR_{ingestion}} + \mathrm{CR_{dermal\ contact}} + \mathrm{CR_{inhalation}} = \mathrm{CDI_{ingestion}} \times \mathrm{SFO} + \mathrm{CDI_{dermal\ contact}} \times \frac{\mathrm{SFO}}{\mathrm{GIABS}} + \mathrm{CDI_{inhalation}} \times \mathrm{IUR} \quad (6)$$

$$\mathrm{TCR} = \sum \mathrm{CR_x} \quad (7)$$

…where SFO is the corresponding oral cancer slope factor, $(mg/kg\text{-}day)^{-1}$, and IUR is the corresponding inhalation unit risk, $(\mu g/m^3)^{-1}$.

Due to the lack of the RfC and IUR data of most OPEs, the health risk assessment of OPEs via inhalation are not calculated in previous studies [1, 23, 24]. Similarly, the risk caused by inhalation is not considered in this study. In addition, the RfD of TPrP, TiBP and EHDPP were not reported in previous literature, so the unobserved adverse effect level (NOAEL) of these three OPEs were used to calculate the RfD. The calculated method is the NOAEL divided by 1000 [23]. In short, the RfD of TEP, TPrP, TiBP, TBEP, TCPP, TDCP, TPhP, EHDPP, TCrPs and TPPO was 0.125 [8], 0.009 [25], 0.1 [26], 0.02 [23], 0.01 [21], 0.02 [21], 0.07 [23], 0.005 [27], 0.02 [7] and 0.02 mg/kg-day [21], respectively. The SFO of TnBP, TEHP and TCEP was 0.009, 0.0032 and 0.02 $(mg/kg\text{-}day)^{-1}$, respectively [21].

Among the 13 OPEs, TCEP, TDCP and TBEP are considered to be potentially carcinogenic [28], but due to the lack of their SFO, TDCP and TBEP are considered as a non-carcinogen to assess their risks in a previous study [24]. It is worth noting that USEPA released the SFO of TnBP, TEHP and TCEP [21]. Therefore, the carcinogenic risk of TnBP, TEHP and TCEP as well as the non-carcinogenic risk of other OPEs including TDCP and TBEP were assessed in this study.

Parameters Sensitivity Analysis

In equations (1)-(7), the suitable constant values of parameters were used to calculate the health risk. However, some parameters were uncertain and could lead to great effect on the health risk assessment. In order to evaluate parameter sensitivity, we applied Crystal Ball 11.1 software, which is based on Monte Carlo stochastic simulation. In this study, the parameters such as IR, SA, AF, ABS, EF and BW were considered as the random variables. Their values are shown in Table S1.

Results and Discussion

Concentrations of OPEs in Topsoil Samples

The ∑OPEs in urban topsoils of Shenyang varied from 0.0387 to 0.9522 mg/kg -dw, and the average and median concentration were 0.2298 and 0.1562 mg/kg -dw, respectively (Table 2). Of 13 OPEs, TiBP has the highest proportion, and the average and median concentration were 0.1003 and 0.0476 mg/kg -dw, respectively. The proportion of TPrP is the lowest, and the average and median concentrations were 0.0008 and 0.0003 mg/kg -dw, respectively. The coefficient of variation of each OPE content is higher than 0.1, which means that the spatial variability of soil OPEs content is large in the sampling area. This indicates that the anthropogenic factors that influence the content of OPEs in soils have obvious spatial differences.

The inverse distance weighted (IDW) in ArcGIS was used to describe the spatial distribution of OPEs in topsoils of the central area of Shenyang (Fig. 2). The concentrations of OPEs are high in east and west Shenyang, but low in the north and south, which may be related to the regional economic structure of Shenyang. Dadong and Tiexi districts are the industrial bases of Shenyang – especially Tiexi, which is a heavy industrial base including the auto industry. However, the industry in Shenbei District and Hunnan District is few, service trade is their major sectors. In addition, OPEs are mainly distributed outside the Two Ring Road, which may be why industry is mainly distributed outside the Two Ring Road.

Table 2. Statistical summary of OPE concentrations in soil samples (n=74, mg/kg -dw).

	TEP	TPrP	TiBP	TnBP	TEHP	TBEP	TCEP	TCPP	TDCP	TPhP	EHDPP	TCrPs	TPPO	∑OPEs
Minimum	u.d.l	0.0001	0.0005	0.0006	u.d.l	0.0059	u.d.l	0.0013	0.0015	0.0003	0.0013	u.d.l	0.0086	0.0387
Mean	0.0102	0.0008	0.1003	0.0037	0.0084	0.0146	0.0121	0.0294	0.0133	0.0059	0.0093	0.0107	0.0110	0.2298
Median	0.0051	0.0003	0.0476	0.0021	0.0072	0.0119	0.0076	0.0153	0.0135	0.0026	0.0054	0.0128	0.0099	0.1562
Maximum	0.0521	0.0216	0.6524	0.0258	0.0221	0.0432	0.0561	0.2093	0.0410	0.0795	0.0500	0.0229	0.0226	0.9522
Standard deviation	0.0111	0.0026	0.1362	0.0049	0.0042	0.0083	0.0098	0.0398	0.0072	0.0101	0.0089	0.0063	0.0029	0.1859
Coefficient of variation	1.0844	3.1463	1.3573	1.3116	0.4980	0.5634	0.8098	1.3533	0.5404	1.7294	0.9613	0.5933	0.2622	0.8089
Average of Guangzhou, China (Urban soil)[a]	0.0046	-	-	0.0248	0.0066	0.0958	0.0324	0.0024	0.0144	0.0078	0.0118	0.0484	0.0030	0.2520
Average of Chongqing, China (Urban soil)[b]	0.0057	0.0045	-	0.0035	0.0036	0.0339	0.0113	0.0033	0.0050	0.0048	0.0042	-	-	0.0798
Average of Chengdu, China (Urban soil)[c]	-	-	-	0.0055	0.0024	0.0680	0.0231	-	-	0.0026	-	-	-	0.1015
Average of Osnabrueck, Germany (Urban soil)[d]	-	-	-	-	-	-	0.0050	0.0012	-	0.0036	-	-	-	0.0098
Average of Nepal (Urban soil)[e]	-	-	-	0.0169	0.0145	-	0.0212	0.0215	0.0126	0.0253	0.0232	0.1130	-	0.2482
Average of Bursa, Turkey (Urban soil)[f]	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2710
Average of Three Gorges Reservoir Region, China (Farmland soil)[g]	0.0002	0.0013	-	0.0035	0.0075	0.0001	0.0012	0.0069	0.0003	0.0002	0.0492	0.1960	-	0.2663
Average of Bui Dau, Vietnam (Farmland soil)[h]	-	-	-	-	-	-	-	-	-	0.0100	-	0.0023	-	0.0123
Average of Bursa, Turkey (Farmland soil)[f]	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0410
Average of Hebei, China (Site soil / plastic waste treatment sites)[j]	-	-	0.0470	0.0220	-	0.2000	0.0920	0.0210	-	0.0260	0.0110	0.1190	-	0.5380
Average of Bui Dau, Vietnam (Site soil / E-waste recycling workshop)[h]	-	-	-	-	-	-	0.0040	0.0190	0.0210	0.6200	0.0240	0.0250	-	0.7130

u.d.l, under detection limit. [a] Data taken from Cui et al. (2017); [b] Data taken from He et al. (2017a); [c] Data taken from Yin et al. (2016); [d] Data taken from Mihajlović et al. (2011); [e] Data taken from Yadav et al. (2017); [f] Data taken from Kurt-karakus et al. (2017); [g] Data taken from He et al. (2017b); [h] Data taken from Matsukami et al. (2015); [j] Data taken from Wan et al. (2016).

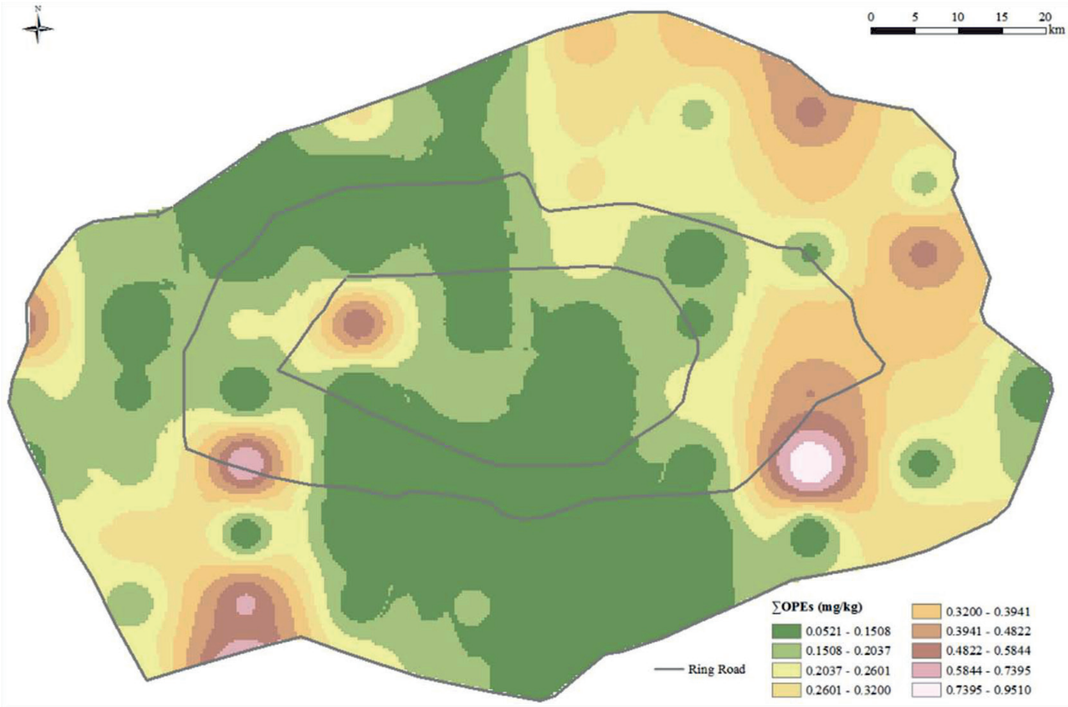

Fig. 2. Spatial distribution of OPEs in Shenyang urban topsoils.

The comparison with the concentration of OPEs in urban soils of different cities, farmland soils and site soils are shown in Table 2. Compared with other cities in China, the average concentration of OPEs in topsoils of central Shenyang is more than two times that of Chongqing and Chengdu, but similar to Guangzhou [9, 29, 30]. Compared with cities in other countries, the average concentration of OPEs in topsoils of central Shenyang is similar to Nepal and Bursa (Turkey), but significantly higher than that of Osnabrueck (Germany) [31-33]. Compared with farmland soils, the concentration of OPEs is higher in urban soils [33, 34]. However, there are exceptions, such as Three Gorges Reservoir Region of China, where the concentration of OPEs is obviously higher than other farmland soils, but similar to urban soils [35]. Compared with site soils, due to site soils being located around the pollution source, the concentration of OPEs in site soils is high, at about 3 to 4 times as much as urban soils [2, 34].

Carcinogenic Risk

The carcinogenic risks of these three carcinogenic OPEs exposed via ingestion and dermal contact for adults and children were assessed; the results were shown in Table 3. For adults and children, the TCR ranged from 2.30×10^{-11} to 4.16×10^{-10} and 2.21×10^{-11} to 4.00×10^{-10}, respectively. The carcinogenic risks for adults were slightly higher than children. However, they all were far less than the acceptable level (10^{-6}) of the carcinogenic risk [22]. These indicated that the cancer risk of OPEs can be negligible. In the two exposure pathways, the risk which is exposed by dermal contact is higher than ingestion, but not much higher, indicating that dermal contact and ingestion are equally important exposure pathways. Among the three carcinogenic OPEs, the risk of TCEP is the highest, accounting for more than 80% of TCR. Therefore, the pollution of TCEP should be focused on.

To intuitively evaluate the carcinogenic risks of OPEs in the study area, the IDW in ArcGIS was used to describe the carcinogenic risks of OPEs in Shenyang (Fig. 3a). The carcinogenic risks have evident characteristics of regional distribution. The carcinogenic risks in the northeast and southwest corner of Shenyang are higher while the risks in the north and south are lower. The spatial distribution of carcinogenic risks of adults is similar to children (Fig. 3a) and Fig. S1a). The spatial distribution of carcinogenic risks is also similar to OPE concentrations.

Non-Carcinogenic Risk

The non-carcinogenic risks that are exposed by ingestion and dermal contact for adults and children were assessed when the RfD of the 10 non-carcinogenic OPEs were obtained, the results are shown in Table 3. For adults and children, the THI ranged from 1.61×10^{-6} to 2.84×10^{-5} and 6.17×10^{-6} to 1.09×10^{-4}, respectively. The non-carcinogenic risks of children were higher than adults, about 5 times, but far below the acceptable level (1) of the non-carcinogenic risks [22], indicating that the OPEs in urban topsoils of Shenyang will not pose non-carcinogenic risks for humans. In the two exposure pathways, the risk exposed by dermal contact is higher than ingestion, but not much higher, indicating

Table 3. Carcinogenic risk and non-carcinogenic hazard quotient of the target compounds.

Compounds	Adults						Children					
	Ingestion		Dermal contact		CR/HQ		Ingestion		Dermal contact		CR/HQ	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
TnBP	5.51×10^{-13}	2.42×10^{-11}	1.10×10^{-12}	4.83×10^{-11}	1.65×10^{-12}	7.26×10^{-11}	7.48×10^{-13}	3.29×10^{-11}	8.40×10^{-13}	3.69×10^{-11}	1.59×10^{-12}	6.98×10^{-11}
TEHP	0.00	7.38×10^{-12}	0.00	1.47×10^{-11}	0.00	2.21×10^{-11}	0.00	1.00×10^{-11}	0.00	1.12×10^{-11}	0.00	2.12×10^{-11}
TCEP	0.00	1.17×10^{-10}	0.00	2.34×10^{-10}	0.00	3.51×10^{-10}	0.00	1.59×10^{-10}	0.00	1.78×10^{-10}	0.00	3.37×10^{-10}
TCR					2.30×10^{-11}	4.16×10^{-10}					2.21×10^{-11}	4.00×10^{-10}
TEP	0.00	1.27×10^{-7}	0.00	2.53×10^{-7}	0.00	3.80×10^{-7}	0.00	6.89×10^{-7}	0.00	7.72×10^{-7}	0.00	1.461×10^{-6}
TPrP	4.17×10^{-9}	7.32×10^{-7}	8.33×10^{-9}	1.46×10^{-6}	1.25×10^{-8}	2.19×10^{-6}	2.27×10^{-8}	3.98×10^{-6}	2.54×10^{-8}	4.45×10^{-6}	4.81×10^{-8}	8.43×10^{-6}
TiBP	1.39×10^{-9}	1.99×10^{-6}	2.78×10^{-9}	3.96×10^{-6}	4.17×10^{-9}	5.95×10^{-6}	7.57×10^{-9}	1.08×10^{-5}	8.48×10^{-9}	1.21×10^{-5}	1.61×10^{-8}	2.29×10^{-5}
TBEP	9.05×10^{-8}	6.57×10^{-7}	1.80×10^{-7}	1.31×10^{-6}	2.71×10^{-7}	1.97×10^{-6}	4.91×10^{-7}	3.57×10^{-6}	5.50×10^{-7}	4.00×10^{-6}	1.04×10^{-6}	7.57×10^{-6}
TCPP	4.01×10^{-8}	6.37×10^{-6}	8.00×10^{-8}	1.27×10^{-5}	1.20×10^{-7}	1.91×10^{-5}	2.18×10^{-7}	3.46×10^{-5}	2.44×10^{-7}	3.88×10^{-5}	4.61×10^{-7}	7.34×10^{-5}
TDCP	2.30×10^{-8}	6.24×10^{-7}	4.59×10^{-8}	1.24×10^{-6}	6.89×10^{-8}	1.87×10^{-6}	1.25×10^{-7}	3.39×10^{-6}	1.40×10^{-7}	3.79×10^{-6}	2.65×10^{-7}	7.18×10^{-6}
TPhP	1.35×10^{-9}	3.46×10^{-7}	2.69×10^{-9}	6.90×10^{-7}	4.04×10^{-9}	1.04×10^{-6}	7.33×10^{-9}	1.88×10^{-6}	8.21×10^{-9}	2.10×10^{-6}	1.55×10^{-8}	3.98×10^{-6}
EHDPP	7.96×10^{-8}	3.04×10^{-6}	1.59×10^{-7}	6.07×10^{-6}	2.38×10^{-7}	9.11×10^{-6}	4.32×10^{-7}	1.65×10^{-5}	4.84×10^{-7}	1.85×10^{-5}	9.17×10^{-7}	3.50×10^{-5}
TCrPs	0.00	3.48×10^{-7}	0.00	6.95×10^{-7}	0.00	1.04×10^{-6}	0.00	1.89×10^{-6}	0.00	2.12×10^{-6}	0.00	4.01×10^{-6}
TPPO	1.30×10^{-7}	3.43×10^{-7}	2.60×10^{-7}	6.85×10^{-7}	3.90×10^{-7}	1.03×10^{-6}	7.08×10^{-7}	1.86×10^{-6}	7.92×10^{-7}	2.09×10^{-6}	1.50×10^{-6}	3.95×10^{-6}
THI					1.61×10^{-6}	2.84×10^{-5}					6.17×10^{-6}	1.09×10^{-4}

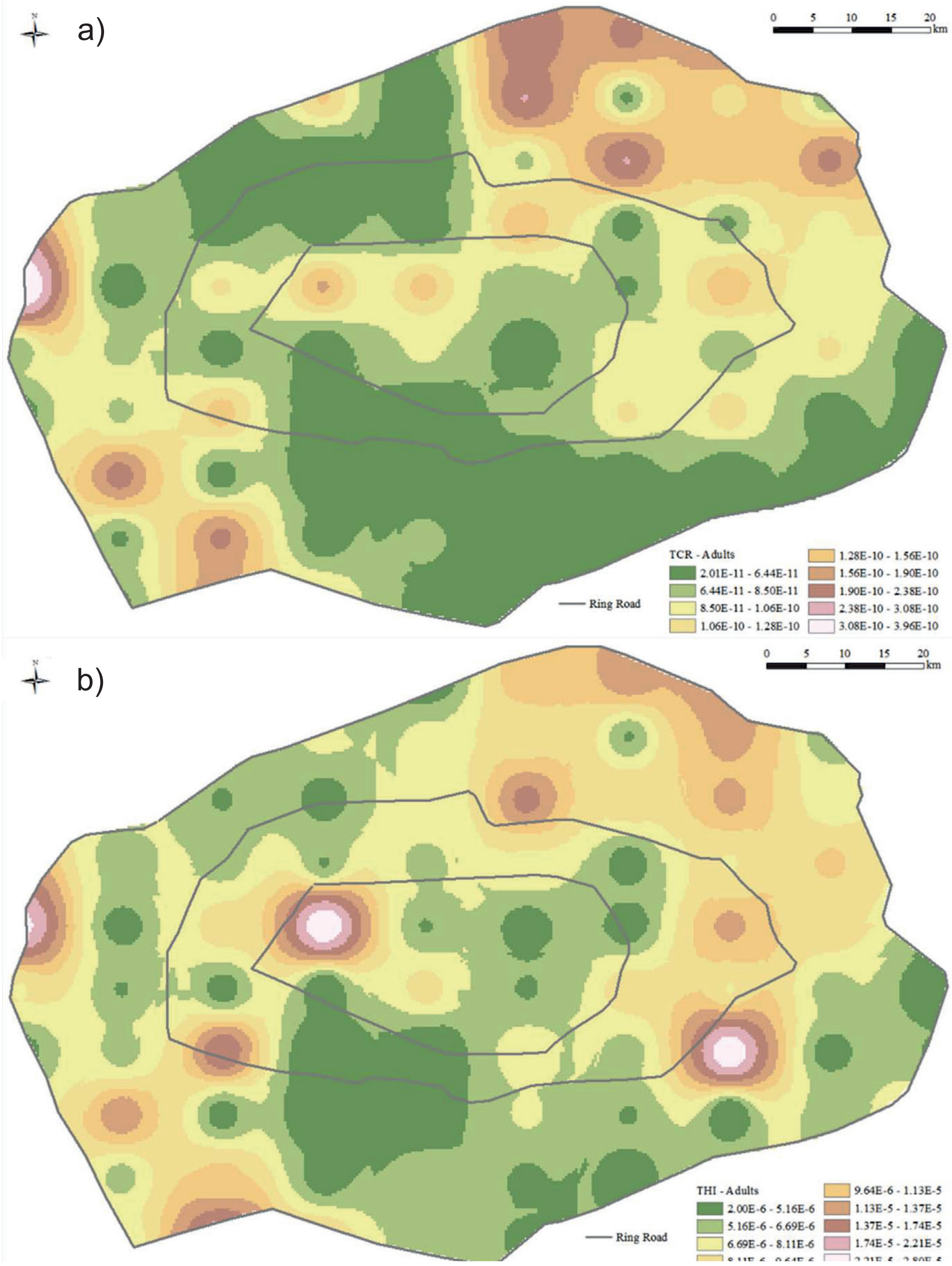

Fig. 3. Carcinogenic risks a) and non-carcinogenic risks b) of adults in Shenyang.

that dermal contact and ingestion are equally important exposure pathways. Among the 10 non-carcinogenic OPEs, the highest risk is TCPP, followed by EHDPP and TiBP. The risks of these three OPEs were obviously higher than other OPEs. Therefore, the pollution of TCPP, EHDPP and TiBP should be focused on.

The IDW in ArcGIS was applied to describe the non-carcinogenic risks of OPEs in Shenyang (Fig. 3b). The non-carcinogenic risks of OPEs were relatively evenly distributed in Shenyang, the areas which have high and low risks were fewer, and the non-carcinogenic risks in most areas were at the intermediate level. The spatial distribution of non-carcinogenic risks of adults is similar to children (Fig. 3b and Fig. S1b), but different to the spatial distribution of carcinogenic risks.

Parameter Sensitivity

A quantitative sensitivity analysis was used to assess the variability and uncertainty of parameters in the different exposure pathways, which can affect risk assessment. The results of sensitivity analysis for carcinogenic risk and non-carcinogenic risk are shown in Fig. 4 and Fig. S2, respectively. OPE concentration is the most sensitive parameter that contributed the largest to the total variance of risk. For carcinogenic risk, the concentration of TCEP is the most influential variable, which contributed 89.52 and 88.42% of the total variance of carcinogenic risk assessment for adults and children, respectively. For non-carcinogenic risk, the concentrations of TCPP, EHDPP and TiBP were the

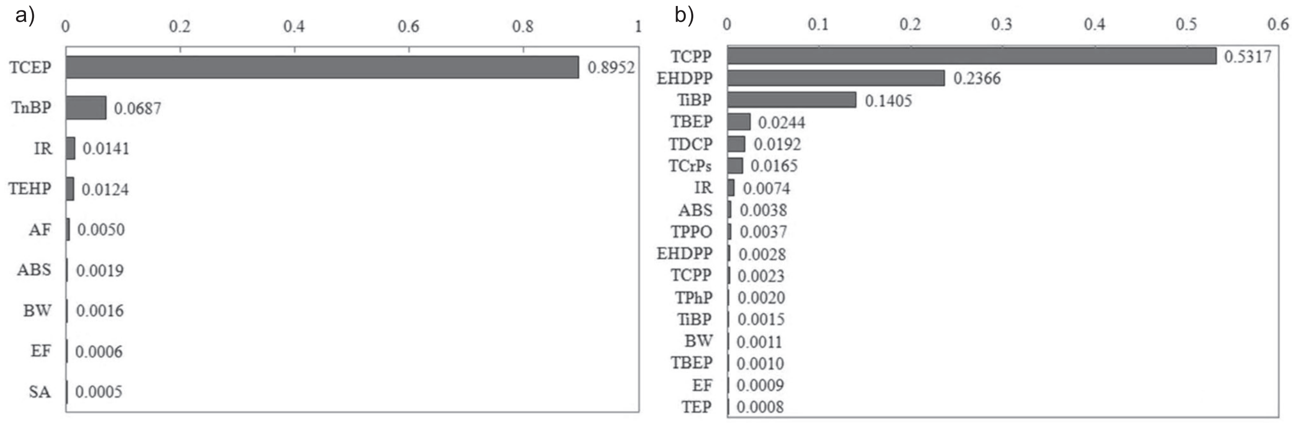

Fig. 4. Sensitivity analysis for carcinogenic risk a) and non-carcinogenic risk b) for adults.

most influential variables, which contributed 53.17, 23.66 and 14.05% of the total variance of non-carcinogenic risk assessment for adults respectively, and contributed 52.6, 25.14 and 13.34% of the total variance of non-carcinogenic risk assessment for children respectively. The results were similar to the previous studies about other pollution, which suggested that the concentration of pollution is the most sensitive parameter in risk assessment [36]. Thus, controlling the concentration of OPEs, especially TCEP, TCPP, EHDPP and TiBP, is the most effective way to mitigate health risk.

Conclusions

We investigated the human health risk assessment of 13 OPEs in urban topsoils of Shenyang. ∑OPE concentrations are high in the east and west, but low in the north and south. OPE pollution levels are higher than farmland soils and lower than site soils, but similar to other urban soils. The carcinogenic and non-carcinogenic risks are far less than the acceptable level, which indicated that the OPEs in urban topsoils of Shenyang will not pose adverse effects on humans. Among 13 OPEs, TCEP is the most important carcinogen, and TCPP, EHDPP and TiBP are the most important non-carcinogens. The concentration of OPEs contributed the largest to the total variance of risk, which indicated that it is the most sensitive parameter. Among them, TCEP is the most influential variable for carcinogenic risk, while TCPP, EHDPP and TiBP are the most influential variables for non-carcinogenic risk.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Materials

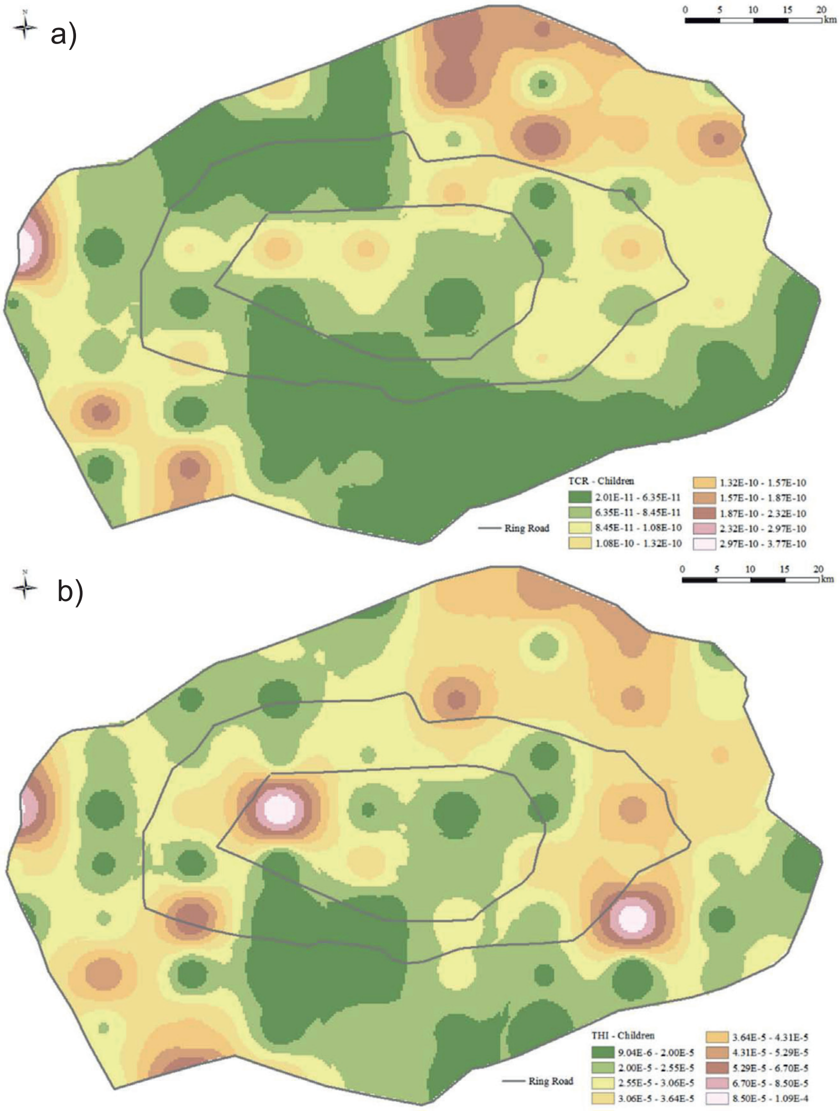

Fig. S1. Carcinogenic risk a) and non-carcinogenic risk b) of children in Shenyang.

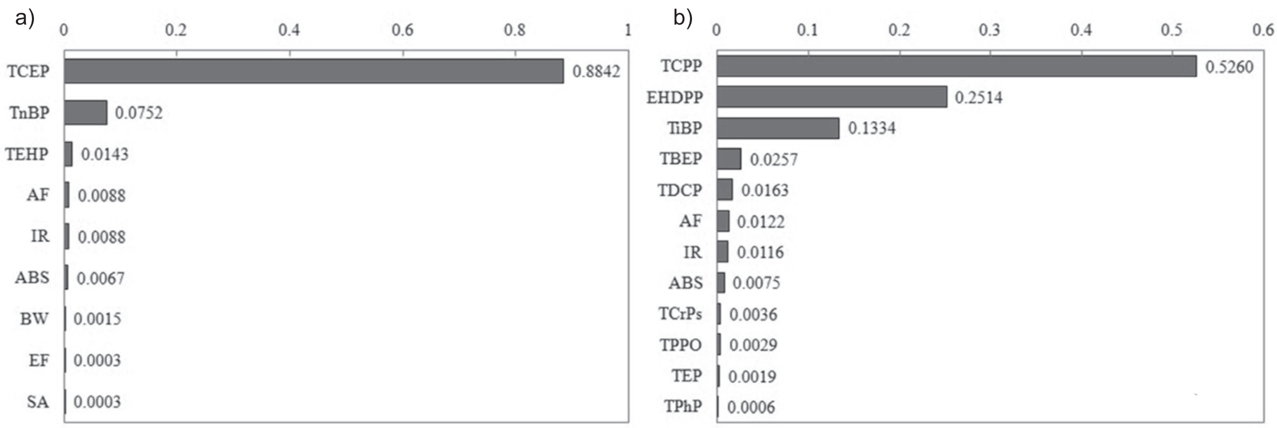

Fig. S2. Sensitivity analysis for carcinogenic risk a) and non-carcinogenic risk b) for children.

Table S1. Values of random variables.

Parameters	Units	Distribution[a]	Value	
			Adults	Children
IR[b]	mg/day	Log-normal	(26.95, 1.88)	(23.85, 1.88)
SA[c]	cm^2	Log-normal	(3067, 1.06)	(2196, 1.08)
AF[c]	mg/cm^2	Log-normal	(0.02, 2.668)	(0.04, 3.404)
ABS[c]	unitless	Log-normal	(0.13, 1.26)	(0.13, 1.26)
EF[c]	day/year	Log-normal	(252, 1.01)	(252, 1.01)
BW[c]	kg	Log-normal	(59.78, 1.07)	(36.24, 1.05)

[a] For log-normal distribution, the geometric mean and geometric standard deviation were expressed as (gm, gsd).
[b] Data taken from Chen et al. (2012).
[c] Data taken from Chen and Liao (2006).

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