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Risk assessment of polychlorinated biphenyls and heavy metals in soils of an abandoned e-waste site in China

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ABSTRACT

Risk assessment of abandoned e-waste recycling areas received little attention. Herein, we report the concentrations of 16 PCBs and 7 heavy metals in soils near an abandoned e-waste recycling plant in Taizhou, China. Our data showed that levels of tri-, tetra-, penta-, hexa-PCBs were 9.01, 5.56, 12.93, 3.13 mg/kg, and Pb, Cd, Cu were 6082.9, 42.3, 2364.2 mg/kg soil. Cd was the most prevalent contaminant with Nemerow index value of 44.3. Contaminants have been transported from the abandoned site to nearby areas. The ecology risk assessment based on the high toxicological effect in Chinese hamster ovary cells and earthworms showed that both PCBs and heavy metal residue pose high risk to the ecosystem. Hazard quotient showed that Pb, Cd, Hg and Cu pose high health risks for adults and children. Our results recommended a full examination of the risk and regulatory compliance of abandoned e-waste recycling areas in the future.

1. Introduction

The management of electronic wastes (e-wastes) has received a great deal of attention among scientists and the general public for several decades (Tanskanen, 2013). The disposal costs of e-wastes must be balanced against the environmental benefit, which often results in a heated public debate. In recent years, numerous studies have revealed that toxicants, including heavy metals and polychlorinated biphenyls (PCBs), were ubiquitous in the sediment, air, and aquatic biota around e-waste regions (Tian et al., 2011; Wang et al., 2011a, 2011b; Zheng et al., 2011). Organisms exposed to these pollutants were reported to have a wide range of adverse effects, including acute effects (Guo et al., 2012), endocrine disruption (Pliskova et al., 2005), reproductive dysfunction (McAuliffe et al., 2012), and cancer (Nomiyama et al., 2011). Therefore, much effort has been made to alleviate the increasing environmental burden from the improper disposal of e-wastes, such as amended laws, enacted regulations, and regional e-waste disposal centers with advanced technologies.

In order to deal with the worsening e-waste situation, China has recently established several legislation approaches for the management of e-wastes. The regional e-waste disposal center is proved to be a more effective measure to reduce the pollution from the illegal e-waste dismantling. However, the established disposal center left many small-scale recycling regions abandoned, such as workshops. New problems emerged for these abandoned regions without any further disposal. It is reported that extremely high levels of heavy metals and persistent halogenated compounds have been detected in abandoned regions after primitive recycling operations (Lopez et al., 2011; Man et al., 2010). To the best of our knowledge, available information is limited on the distribution and environmental risk of the main pollutants in abandoned e-waste recycling areas. In China Taizhou is one of these cities with the largest numbers of e-waste recycling centers. In recent years, e-waste recycling in Taizhou has been mainly limited to several disposal centers as the established regulated management system by Chinese government (Zhang et al., 2012). Consequently, large numbers of scattered e-waste recycling workshops were abandoned without adequate attention and subsequent management, which in fact has facilitated the release of hazardous chemicals into the surroundings. Given the potential adverse impacts on non-target organisms and local residents, understanding the concentration and composition of the pollutants and their environmental risks in abandoned regions is an urgent concern.

In this study, we collected soil samples from a site where an abandoned e-waste recycling plant in Taizhou, Zhejiang province had been operating for more than five years before its operation ceased in 2008. The levels of PCBs and heavy metals were investigated in and near the abandoned e-waste recycling site. The

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integrated ecological risks to animals and humans were evaluated using an earthworm mortality assay (*in vivo*), cytotoxicity to Chinese hamster ovary (CHO) cell lines (*in vitro*) and the non-carcinogenic exposure risks to adults and children. The data will be valuable to scientists and policy-makers to comprehend the legislation to deal with the regulation of e-wastes.

2. Materials and methods

2.1. Sample collection

The abandoned e-waste recycling plant is located in Taizhou, Zhejiang province, China (N28°31′31.33″, E121°22′5.18″) (Fig. S1). The distance between each sampling site was 100 m. The northern, southern, and eastern directions of the abandoned recycling plant were a concrete path or residential area and no soil could be collected in that area. Therefore we only obtained soil samples nearby this abandoned site in the western direction. According to the boundary of the fence around this abandoned e-waste recycling plant, these areas were classified into two groups: the abandoned e-waste recycling site and the area surrounding the abandoned e-waste recycling site. In total, 32 sampling sites were located around the plant, and 16 sampling sites were located within the abandoned plant. Top soil samples (0–15 cm from the surface) were collected, with each soil sample consisting of three sub-samples. After the gravel was removed, all of the samples were placed into pre-washed aluminum jars and immediately stored at −20 °C until further analysis.

2.2. Heavy metals analysis

The heavy metals in soil samples were quantified as previously described with minor modifications (Niu et al., 2013). Briefly, 0.1 g of soil was digested with HNO_3, $HClO_4$ and HF ($v/v/v$ = 3:1:1) in a 100 mL flask at 200 °C for 2 h. Then, a high-performance microwave digestion unit was employed to digest the samples at 180 °C for 7 h. After digestion and cooling, the mixture was washed with 1% HNO_3 three times and diluted to 50 mL using deionized water. Finally, inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500a, Agilent, Santa Clara, California) was used for metals analysis.

2.3. Sample extraction and analysis of PCBs

Approximately 5 g of the air-dried soil sample was homogenized in a Soxhlet apparatus with dichloromethane (DCM): hexane = 3:7 (v/v) for 24 h. Copper powder was added to remove the sulfur. Then, the extract was concentrated to approximately 1 mL after the solvent was exchanged with hexane. Purification procedures were conducted through a multi-layer silica gel column containing, from top to bottom, anhydrous Na_2SO_4 with 10% (w/w) silver nitrate silica gel (6 cm), neutral silica gel (2 cm, 3% deactivated), 33% sodium hydroxide silica gel (6 cm), neutral silica gel (2 cm), 44% sulfuric acid silica gel (6 cm), neutral silica gel (4 cm) and an eluant of 100 mL hexane/DCM (9:1, v/v). Finally, the eluant was concentrated to approximately 1 mL using a gentle stream of N_2. A known amount of $^{13}C_{12}$-labeled PCB 101 was added as an internal standard prior to GC–MS analysis.

A GC-EI-MS device (Agilent 7890) with an HP-5 capillary column (30 m × 0.25 mm × 0.32 μm, J&W Scientific Co., CA, USA) was used to identify the PCBs. The initial oven temperature was set at 60 °C, where it was held for 1 min, increased at 10 °C/min to 160 °C, held 1 min, increased at 2 °C/min to 180 °C, increased at 0.5 °C/min to 185 °C, held 1 min, increased at 1 °C/min to 190 °C, held 1 min, increased at 2 °C/min to 260 °C, and held for 5 min. The temperatures of the ion source and quadrupole were set at 230 °C and 150 °C, respectively (Yang et al., 2012).

2.4. Quality assurance and quality control

A method blank (solvent), a spiked blank (standards spiked into solvent) and a matrix spike (standards spiked into soils) were processed with each batch of 10 samples, and no target compounds were detected. The method detection limits (MDLs) for PCBs ranged from 0.004 to 0.015 ng/g. The recovery of the analyses ranged from 73% to 106%.

For heavy metals, all glassware was soaked in 10% HNO_3 for 12 h before use. The samples were prepared in an airtight environment to avoid volatilization and cross-contamination among samples. Blank samples and two reference soils obtained from the Chinese National Standard Soil Bank were included with every 10 samples to validate the accuracy of the metal analysis.

2.5. Cell culture and treatment

The CHO cell line was obtained from the cell bank at the Chinese Academy of Sciences (American Type Culture Collection, ATCC). The cells were grown in RPMI-1640 medium in an incubator at a temperature of 37 °C with 5% CO_2. After the cells reached logarithmic confluence, they were seeded in 96-well plates (Coaster, 5×10^4 cells/mL). The following day, the cells were exposed to experimental medium (containing 1% fetal bovine serum, FBS) with or without soil extract. After 24 h, 40 μL CellTiter 96 Aqueous One Solution (Promega) was added to the experimental medium. After 2-h incubation at 37 °C, the OD_{490} was measured on a Bio-Rad Model microplate reader (Bio-Rad Laboratories, Hercules, CA, USA).

2.6. Earthworm mortality assay

Age-synchronized adult earthworms (*Eisenia foetida*) were obtained from the Active Central Earthworm Breeding Farm of Zhejiang University. The earthworm mortality tests were performed according to OECD (2004). All tests were conducted with the control or samples from Taizhou area at 26 ± 2 °C. After an incubation of one or two weeks, the endpoint of the earthworm survival was recorded.

2.7. Non-carcinogenic health risk estimation

The non-cancer hazard is expressed as a ratio of the concentration of a toxicant in the environmental matrix to the recommended safety level of that compound, termed as hazard quotient (HQ). The equations to estimate HQ are as follows:

$$HQ = ADD/RfD,$$
$$ADD = C \times IR \times ED \times EF/BM \times AT$$

where the ADD is the average daily dose, RfD is reference dose, C is the mean metal concentration (mg/kg), IR is the conservative estimates of ingestion rates (mg/day), ED is exposure duration (years), BM is the body weight (kg), EF represents the exposure frequency (days/year), and AT is average exposure time (days).

2.8. Statistical analysis

Statistical analyses were conducted using PASW Statistics 18. Pearson regressions were used to test the correlations between contaminants. The effects of sampling sites on the cell viability and earthworm mortality were evaluated by the analysis of variance (ANOVA). Principal component analysis (PCA) was performed with factor analysis in PASW Statistics 18. The values were recorded as the mean ± standard error. The significance level was set at $p < 0.05$.

3. Results

3.1. Concentrations of PCBs and metals

The statistical descriptions of the PCBs and metals from the soil collected from the two areas are summarized in Table 1. To evaluate the extent of metal contamination, we introduced the Nemerow index (Table 2). In general, the concentration of pollutants in the abandoned area was remarkably high. The nearby area was also contaminated with PCBs and metals.

The samples were analyzed for a total of 16 PCBs, including 7 dioxin-like PCBs (PCB 123, 118, 114, 105, 126, 167, 156, 169, and 189). For a comparison purpose, the PCBs was categorized into five classes. As described in Fig. 1, the compositions of PCBs were similar in both the abandoned area and the nearby area. The lower chlorinated congeners such as tri-, tetra-, and penta-PCB were the abundant pollutants, accounting for 60% of the total PCBs. The penta-PCB was the most prevalent homolog, and hepta-PCB was the least prevalent. The chemical concentrations in Table 1 show that the mean values of tri-, tetra-, penta-, hexa- and hepta-PCB were 9012.3, 5557.4, 12928.6, 3129.4, and 0.6 μg/kg, respectively, in the abandoned area. In China, no quality standard has been set for PCBs in soils. Nevertheless, the residual PCB levels in the abandoned area exceeded the less stringent Canadian soil guideline for residential areas (1300 μg/kg) (Canadian Environmental Quality Guidelines, 2003). Although the chemical levels in the nearby area were 50–80 fold lower than those in the abandoned area, these levels were several times higher than the allowable level set by the former USSR Ministry of Health (60 μg/kg) (Bobovnikova et al., 1993), indicating high level of contamination.

The metal concentrations shown in Table 1 indicate that both areas were contaminated with Pb, Cd, Cr, Zn, As, Hg, and Cu. The mean values of Pb, Cd, Cr, Zn, As, Hg, and Cu were 6082.9, 42.3, 771.5, 5995.6, 36.6, 4.1, and 2364.2 mg/kg, respectively. Near abandoned e-waste cycling area, the average levels of these metals were 167.4, 2.2, 69.5, 275.5, 5.3, 0.8, and 157.3 mg/kg, respectively.

The Nemerow index, which represents the comprehensive pollution, was introduced to evaluate the soil quality. As shown in