

Distribution of Phthalate Esters in Soil of E-Waste Recycling Sites from Taizhou City in China

W. L. Liu · C. F. Shen · Z. Zhang · C. B. Zhang

Received: 7 January 2009 / Accepted: 26 February 2009 / Published online: 17 March 2009
© Springer Science+Business Media, LLC 2009

Abstract In recent years, increasing concern has surrounded the consequences of improper electric and electronic waste (e-waste) disposal. In this paper, Phthalate esters (PAEs) including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), Di-(2-ethyl-hexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DnOP) in the e-waste soils were collected and analyzed from sites Fengjiang, Nanshan and Meishu in Taizhou city. The result showed that the total PAEs concentrations ranged from 12.566 to 46.669 mg/kg in these three sites. DEHP, DBP and DEP were the major phthalates accounting for more than 94% of total phthalates studied. Comparing to the results from other studies, the e-waste soils from Taizhou city were severely contaminated with PAEs.

Keywords E-waste · Soil · Phthalate esters (PAEs) · Chemical analysis

Electric and electronic waste (e-waste) becomes the most rapidly growing waste problem in the world. Much e-waste is being exported to developing countries, and especially for East and South Asia (UNEP 2005). Taizhou, a city of south China, one of the largest e-waste disposal centers in China, which is involved in recycling for many years. These extremely hazardous and dangerous e-waste “recycling”

operations render the air, water and soil. Persistent toxic substances such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) have been found in e-waste recycling soils (Shen et al. 2008).

Phthalate esters (PAEs) are industrial chemicals that are widely used as plasticizers in polyvinyl chloride resins. They can be found at measurable concentrations all over the world due to high production volumes and an almost continuous release into the environment. PAEs also can be found in leaching from piles of wires, as well as in the ash precipitation caused by open burning of electric wires. The US Environmental Protection Agency (EPA) and China classified the commonly occurring phthalates as priority pollutants and endocrine disrupting compounds. But up to now, we have not found studies about PAEs in e-waste soil. The major purpose of this study is to investigate the concentrations, compositions and distributions of 5 PAEs in e-waste soil in Taizhou city.

Materials and Methods

The standards of DMP, DEP, DBP, DEHP and DnOP at 1,000 µg/mL each, and surrogate standard, diphenyl isophthalate in 500 µg/mL, internal standard, methyl benzoate, acquired initially as a solid of 99% purity, were purchased from ULTRA Scientific. All solvents were of analytical purity (Tiantong Chemical Factory, China). Materials were prepared according to Cai et al. (2005) method.

Nine soil samples were collected from three different e-waste disposal locations at Fengjiang (FJ), Nanshan (NS) and Meishu (MS) sites, in Taizhou city, respectively, in March 2006. At each sampling location, triple samples were collected at 0, 100 and 200 m away from the disposal center,

W. L. Liu (✉) · Z. Zhang · C. B. Zhang
School of Life Science, Taizhou University, 317000 Linhai,
Zhejiang, China
e-mail: liuwenlidy@yahoo.com.cn

C. F. Shen
Department of Environmental Engineering, Zhejiang University,
310029 Hangzhou, China

where about 10 m far from the verge to avoid road influence. A control sample was collected in a farmland without PAEs pollution. All samples were collected using a pre-cleaned stainless steel scoop into pre-cleaned aluminum foil envelopes. The soils were dried at room temperature, ground to 30 mesh after removing stones and residual roots, and stored in glass bottles at -4°C until further processing. All the results were reported as dried weight.

Sample extraction and fractionation were carried out using Zeng et al. (2005) method. The identification and quantification of PAEs were measured with an Agilent 7890 (United States) GC system equipped with a flame ionization detector and a fused silica capillary HP-5 column ($30\text{ m} \times 0.25\text{ mm i.d.}$, $0.25\text{ }\mu\text{m}$ film thickness). The carrier gas was helium with a flow of 1 mL/min . $1\text{ }\mu\text{L}$ of sample was injected in splitless mode. The injector and detector temperature were 280 and 300°C , respectively. The temperature program was as follows: initial temperature 50°C , from 50 to 280°C at 4°C/min , and finally 280°C for 10 min .

For each batch of nine soil samples, Surrogate standards were added to all the samples to monitor matrix effects. The surrogate recoveries were $80.1 \pm 11.7\%$. Recoveries of 5 PAEs ranged from 78.4% to 115% (relative standard deviations $< 13.6\%$) in the spiked blank samples, from 74.6% to 110% (relative standard deviations $< 10.1\%$) in the spiked soil matrix samples. The limit of detection (LOD) for the phthalate esters, estimated as three times response of signal-to-noise of 3:1 in blank sample, ranged from 0.02 mg/kg for DMP to 0.236 mg/kg for DEHP.

Statistical analysis was performed with SPSS 13.0 for Windows (SPSS Inc, Chicago, IL).

Results and Discussion

Of all the samples, the total concentration of phthalates (ΣPAEs) in soils from sites FJ, NS and MS varied from 12.566 to 46.669 mg/kg , which was higher than that in the control. The highest ΣPAEs concentration was found at site FJ, where PAEs may be released from a significant amount of plastics and wires and came into the soil due to human improper e-waste disposal. The relative proportions of the 5 PAEs including DMP, DEP, DBP, DEHP and DnOP in the soils collected from sites FJ, NS and MS were presented in Fig. 1. DEHP, DBP and DEP were the major phthalates accounting for more than 94% of total phthalates studied. Of the commercial PAEs, the share of DEHP was about 50% – 60% (Gómez-Hens and Aguilar-Caballeros 2003). This result was consistent with the commonly reported findings that DEHP and DBP were the dominant components of the PAEs in soil (Cai et al. 2005; Peijnenburg and Struijs 2006). DnOP and DMP were only detected in several soil samples, with

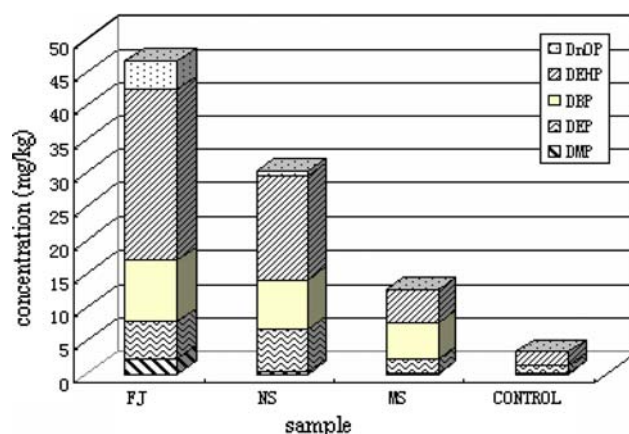


Fig. 1 Concentration and distribution patterns of phthalate esters in different sites

concentrations ranging from $<\text{LOD}$ to 6.080 mg/kg and $<\text{LOD}$ to 2.278 mg/kg , respectively.

The PAEs congener concentration and distribution patterns in distance were presented in Fig. 2. In general, PAEs congener concentration reduced along with the distance away from the disposal centre. However, higher concentrations of DEHP and DBP were found at 100 and 200 m away from the disposal center, respectively. These results agreed with the findings reported by Gómez-Hens and Aguilar-Caballeros (2003). Soluble soil humic materials associate strongly with these higher molecular weight compounds, increasing their apparent water solubility and decreasing their apparent degree of soil sorption (Gómez-Hens and Aguilar-Caballeros 2003).

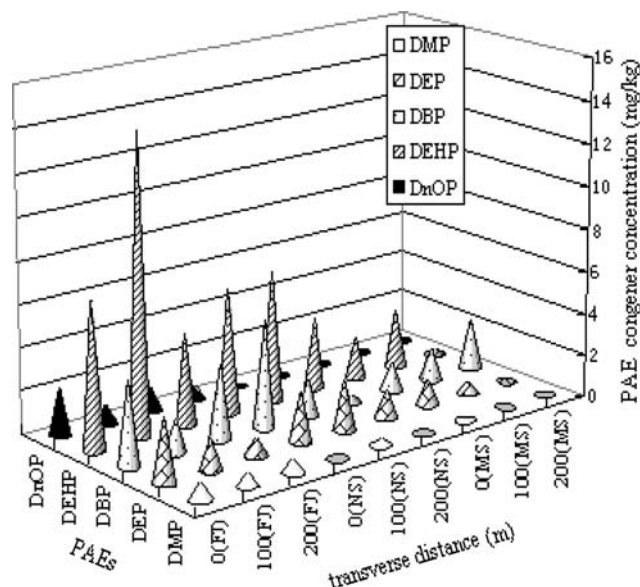


Fig. 2 Relative contributions of 5 PAE congeners in different distance in sites FJ, NS and MS soils

The content of PAEs in soils has been investigated in some countries. Vikelsøe et al. (2002) investigated soil samples in Danish, as a result that total contents of the six PAE compounds ranged from 0.02706 to 0.04628 mg/kg, which was much lower than those measured in this study. Peijnenburg and Struijs (2006) found that DBP and DEHP were 0.006 and 0.0318 mg/kg in soil from Denmark, respectively. Cai et al. (2005) investigated vegetable field soil samples in areas of Guangzhou and Shenzhen of China, the result showed that the total concentration of the six PAE compounds in all soils varied from 3.00 to 45.67 mg/kg, where lots of agricultural plastic films were widely used.

References

- Cai QY, Mo CH, Li YH, Zeng QY, Wang BG, Xiao KE, Li HQ, Xu GS (2005) The study of PAEs in soils from typical vegetable fields in areas of Guangzhou and Shenzhen, South China. *Acta Ecol Sin* 25:283–288
- Gómez-Hens A, Aguilar-Caballos MP (2003) Social and economic interest in the control of phthalic acid esters. *Trends Anal Chem* 22:847–857. doi:[10.1016/S0165-9936\(03\)01201-9](https://doi.org/10.1016/S0165-9936(03)01201-9)
- Peijnenburg WJGM, Struijs J (2006) Occurrence of phthalate esters in the environment of the Netherlands. *Ecotoxicol Environ Saf* 63:204–215. doi:[10.1016/j.ecoenv.2005.07.023](https://doi.org/10.1016/j.ecoenv.2005.07.023)
- Shen CF, Huang SB, Wang ZJ, Qiao M, Tang XJ, Yu CN, Shi DZ, Zhu YF, Shi JY, Chen XC, Setty K, Chen YX (2008) Identification of Ah receptor agonists in soil of e-waste recycling sites from Taizhou area in China. *Environ Sci Technol* 42:49–55. doi:[10.1021/es071162z](https://doi.org/10.1021/es071162z)
- UNEP (2005) E-waste: the hidden side of IT equipment's manufacturing and use. Early warnings on emerging environmental threats no. 5. United Nations Environment Programme, Kenya
- Vikelsøe J, Thomsen M, Carlsen L (2002) Phthalates and nonylphenols in profiles of differently 22 dressed soils. *Sci Total Environ* 296:105–116. doi:[10.1016/S0048-9697\(02\)00063-3](https://doi.org/10.1016/S0048-9697(02)00063-3)
- Zeng F, Chen LX, Cui KY, Zhang G (2005) The determination of phthalate esters in sediment sample by silicagel-alumina column separation and gas chromatography. *Chin J Anal Chem* 33:1063–1067