Occurrence of Phthalate Esters in MSW Landfill Area, Wuhan, China

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***Abstract*—Samples of groundwater, leachates, surface water and soils were collected from 22 sites in the Municipal solid waste landfill area in Wuhan, Central China. Sixteen phthalate esters (PAEs) were detected by gas chromatography (GC). The results showed that there were one or several PAEs in all the samples and the concentrations of total PAEs in groundwater, leachates, surface water, and soils were 0.760~14.14 μg/L, 21.17~139.27 μg/L, 0.63~5.10 μg/L and 0.292 to 7.81μg/g (dw), respectively. The PAEs levels in the groundwater of the MSW landfill in Wuhan were much higher than those of the Jianghan plain. However, the PAEs levels in the other media in this study were similar to those from other places in China. Of the 16 PAEs, DBP, DIBP and DEHP were dominant species in all media samples and only DBP in the groundwater close to the Quality Standard.**

Keywords-Phthalic acid esters; Groundwater; Leachate; Surface water; Soil

I. INTRODUCTION

Phthalate esters (PAEs) are widely used as plasticizers in polyvinyl chloride, polyvinyl acetates, polyurethanes and cellulosics, and as nonplasticizers in consumer products such as paints, adhesives, cardboard, insect repellents, lubricating oils, photographic films, perfumes, and food packaging[1]. Global production of plastics has reached a level of 150 million tons per year [2]. As PAEs do not chemically bind in the polymeric matrix, they can enter into the environment directly and/or indirectly during the production of plastic and plastic material or after disposal. Widespread application of PAE-containing products has leaded that PAEs are ubiquitous in various environmental compartment [3-5].

Recent investigations have shown that several PAEs are environmental hormones [6], which are toxic and harmful to human health, leading to the instability of internal secretions and procreation ability [7]. In general, the acute toxicity of the diesters is low, but ecotoxicological studies have shown that some of the degradation products, i.e. monoesters, may be toxic towards mammals [8, 9]. Since two phthalate ester plasticizers were even detected in the remote marine [10], PAEs contamination has become a serious issue atmosphere at Enewetak Atoll in the North Pacific Ocean arousing much concern.

Many researches carried out in China to investigate the levels of PAEs. It was reported that PAEs concentrations were 0.1~300 μg/L in surface waters and 0.1 ng/g ~ 100 μg/g in sediment [11]. Di-n-butyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) reached 17 and 76 μg/L, respectively, in water samples from 10 Hangzhou water plants [6]. Six PAEs, i.e. dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, DEHP, di-n-octyl phthalate (DOP) and butyl benzyl phthalate (BBP) , amounted to 114.166 μg/g in municipal sludge of Beijing [12]. What's more, the concentration of PAEs was 3.082μg/L in Zhengzhou section of Yellow River [13], and reached 87.23μg/L in Wanjiazai section [14].

Wuhan, with an area of about 8,467 km^2 and a population of about 9.7 million, is the largest urban center in central China, which can produce 5,000~6,000 tons municipal refuse per day. Municipal solid waste landfill may seriously pollute the groundwater aquifer and surface water as they migrate away with leachates [15]. PAEs contamination of lakes in Wuhan City has also been mentioned in recent years. For instance, Zhang et al. [16] and Wang et al. [17] detected 5~9 PAEs in sediment of East Lake (the largest lake in Wuhan City). Xue et al. [18] also determined DBP and DEHP levels in water samples from 6 lakes and 2 rivers in Wuhan City. However, there was still no detailed research on the occurrence of PAEs in different media of landfill area.

The major purpose of this study was to investigate the concentrations, compositions and distributions of 16 PAEs in the groundwater, surface water, leachates, and soil in MSW landfill area in Wuhan, and discuss the transportation of PAEs.

II. MATERIALS AND METHODS

A. Chemicals and materials

Twenty PAEs standard solutions used in this study, including dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), bis (2-methoxyethyl) phthalate (BMEP), bis (4-methyl-2-pentyl) phthalate (BMPP), diamyl phthalate (DAP), bis (2-ethoxyethyl) phthalate (BEEP), hexyl 2-ethylhexyl phthalate (HEHP), dihexyl phthalate (DHP), butyl benzyl phthalate (BBP), bis (2-n-butoxyethyl) phthalate (BBEP), di (2-ethylhexyl) phthalate (DEHP), dicyclohexyl phthalate (DCP), di-n-octyl phthalate (DOP), dinonyl phthalate, benzyl benzoate, diphenyl phthalate (DPP), diphenyl isophthalate

978-0-7695-3563-0/08 $25.00 © 2008 IEEE
DOI 10.1109/ETTandGRS.2008.113

(DPIP) and dibenzyl phthalate (DBZP) were purchased from Dr. Ehrenstorfer GmbH (Germany), namely, including an internal standard(Benzyl benzoate), three surrogate standards (500 ng/μL in acetone) and sixteen PAEs (1000 ng/μL in n-Hexane).

All solvents including methylene chloride, hexane, methanol, acetone, were of HPLC grade and purchased from TEDIA (USA). AccuBOND C_{18} SPE sorbent was purchased from Agilent. Sodium sulfate (anhydrous) was purified by heating at 450 ^{o}C for 4 hours in a SX2-8-13 muffle furnace [Wuhan, China] and cleaned with DCM before use.

To avoid contamination, no plastic equipment was used during sampling and processing. All the glass apparatus were soaked in K_2CrO4 sulfuric acid solution at least 12 hr, rinsed with organic-free reagent water at least 10 times, finally baked at 180 ^{o}C for 4hr. Neutral silica gel (80-100 mesh), and alumina (100-200 mesh) were cleaned with dichloromethane (DCM) using Soxhlet extractor for 72 h, activated at 180°C, 250°C for 12 h, and then deactivated with 3% (w:w) of deionized water, respectively.

B. Samples

Groundwater, surface water, leachates were collected from municipal solid waste landfill R in Wuhan city, Hubei Province, central China, in December 2007. Landfill R was operated during 2003–2007 and engineered with HDPE liners and leachate collection systems.

During sampling and further processing of the samples, precautions were taken to avoid PAEs contamination. At each sampling point, water samples were collected using a clean glass bottle and promptly transferred to 4L dark glass flasks with polytetrafluoroethylene (PTFE)-lined screw-caps. These samples were then transported to the laboratory and immediately filtered with 0.45μm membrane (PL, Millipore). The filtrated samples were stored in pre-cleaned 4L brown glass amber bottles below 4°C until analysis. Soil samples were air-dried, ground, and homogenized after removing stones and residual roots, and stored in aluminum foil bags below 4°C until extraction. The locations of the sampling sites are given in Fig.1.

C. Sample extraction

For water phase, samples were extracted using a 12- port vacuum manifold solid-phase extraction (SPE) system performed according to the EPA Method 3535 and 8061a with modification, respectively. Samples were passed through a 0.45μm membrane and 10μL 100 mg/L surrogate standards (Supelco, USA). Sample extraction and pretreatment were (DPP, DPIP, DBZP) was added to 1 L samples. SPE cartridge (500mg×6mL) (Agilent, USA) was pretreated with 2mL DCM, 1 mL acetone, 2 mL methanol and 2 mL organic-free water, respectively. Water samples were extracted at a flow rate of 4 ml/min. After dried for about 3 minutes, a drying column containing about 8 g of anhydrous sodium sulfate is placed under the SPE cartridge, and a 10ml collection tube below each drip tip of apparatus. Elution solvents (2 mL DCM, 2 mL acetone) were in turn passed through the cartridge. The elution was condensed to 0.2 mL in a N_2 blow equipment (Shanghai, China).

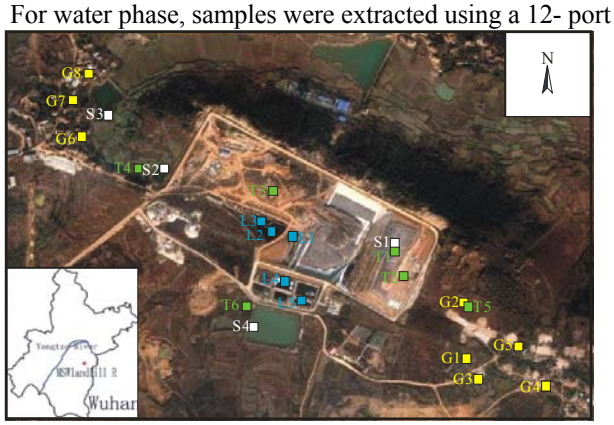

Figure 1. The geographical location of MSW landfill R in the Wuhan city and the sampling sites within landfill R

Soil samples were spiked with surrogate standards, DPP, DPIP, DBZP and extracted with DCM for 24 h at a rate of 4-6 cycles/h using Soxhlet extractor. Activated copper granules were added to the extraction flasks during the extraction to remove elemental sulfur. The extracts were concentrated, flowed through anhydrous sodium sulfate, solvent-exchanged to n-hexane, and further reduced to approximately 1.0 mL using a rotary evaporator. Concentrated extracts were cleaned and fractionated on a 10-mm i.d. 1:2 alumina/silica gel glass column packed, from the bottom to top, with neutral silica gel (12 cm), neutral alumina (6 cm), and anhydrous sodium sulfate (1 cm). The concentrated extracts were added into the column and washed by 40 ml of hexane. Then PAEs were eluted with 40 ml of a mixed solvent of acetone/n-hexane (2:8, v:v). The extracts were concentrated using a rotary evaporator, and reduced to 0.2 ml under a stream of purified N2. Known quantities of internal standard were added to the sample prior to instrumental analysis.

D. Instrumental analysis

The samples were analyzed with an Agilent 6890N gas chromatography (HP, USA), and a DB-5MS capillary column (30 m×250 mm×0.25 mm) (Agilent, USA) for chromatographic separation. The detector temperature was maintained at 280°C. The column temperature program was initiated at 80°C for 1.0 min, increased to 280°C at a rate of 6°C /min, and held for 10 min. Flow rate of the carrier gas N_2 was kept constant at 1.2 mL/min. The extracts (2.0 μl) were injected onto GC in splitless mode with an inlet temperature of 280°C.

E. Quality assurance

For all the samples, a procedural blank and spiked sample consisting of all reagents was run to check for interference and cross contamination. Quantifications of PAEs were done with the calibration curves of which the correlation coefficients were all higher than 0.99. Limits of detection (LODs) of the method with standard solution were 22 ~ 341ng/L under full scan acquisition mode. The spiked recoveries of PAEs were in the range of 61.7%~97.8%.

III. RESULTS AND DISCUSSION

A. PAEs concentrations of groundwater in landfill area

Eight groundwater samples were collected from the lower places than landfill. As shown in Fig.2, the total concentrations of 16 PAEs (Σ16PAEs) in the groundwater samples ranged from 0.760 to 14.14μg/L, which were 10 times higher than that of Jianghan plain (0.08~1.88 μg/L, data have not published). These results indicated that the groundwater was probably polluted by landfill.

B. PAEs concentrations of leachates in landfill area

Fig.3 showed us Σ16PAEs in leachates collected from different sites of MSW landfill. The sum of the 16 PAEs in the leachates ranged from 21.17 to 139.27μg/L, which was similar to that reported previously in Japan and other countries [19-21].

C. PAEs concentrations of surface water in landfill area

PAEs concentrations in the surface water ranged from 0.63 to 5.10μg/L (Fig.4), which approximated to those presented in urban lakes in Guangzhou, but was much lower than those in Yellow River and Wuhan section of the Yangtze River [22-24]. These results indicated that the surface water was not polluted by landfill. The highest Σ16PAEs value was at S3, where was the farthest from landfill and most probably polluted by human agricultural activities.

D. PAEs contents of soil in landfill area

Contents of PAEs in the surface soil samples from different sites of landfill area were illustrated in Fig.5. Significantly high value of Σ16PAE was at T1, where the soil covered the landfill. The Σ16 PAEs ranged from 0.292 to 7.81μg/g -dry weight (dw), with a average value of 1.86 μg/g -dw. These values are similar to that reported in Beijing, East China and South China, but were much lower than those present in urban soils in Guangzhou [25-27]. So the surface soil was not polluted seriously by landfill.

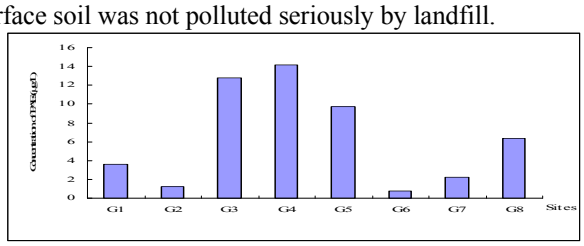

Figure 2. Comparison of Σ16PAEs concentration in groundwater from the MSW landfill(G1-8)

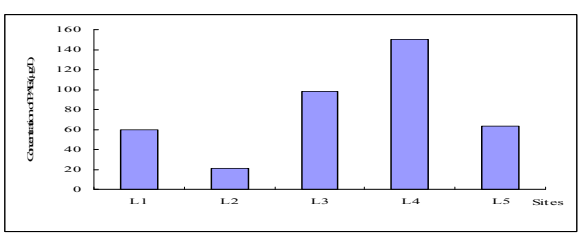

Figure 3. Comparison of Σ16PAEs concentration in leachates from the MSW landfill(L1-8)

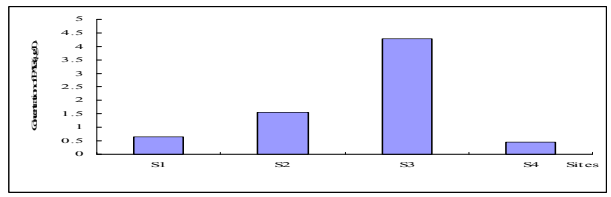

Figure 4. Comparison of Σ16PAEs concentration in surface water from the MSW landfill(S1-8)

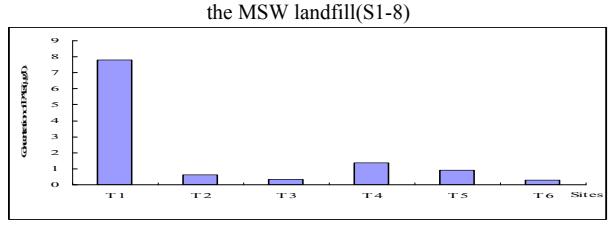

Figure 5. Comparison of Σ16PAEs concentration in soil from the MSW landfill(T1-8)

E. Comparison of PAEs concentrations and species among these media of PAEs

The comparison of PAEs concentrations in the 4 media (Fig.6.) showed that the PAEs concentration in leachates was one or several decuple times higher than that in surface and underground water. Groundwater showed higher concentration than surface water. And the concentrations of PAEs in soil were not significantly higher that that in other places [24-27]. Therefore, PAEs were directly infiltrated into groundwater rather than went through surface water and soil.

The individual PAEs concentrations in the leachates, soil, groundwater and surface water were shown in Fig.7. There were 8 PAEs species were detected in leachates, which were different from the reported [19-21]. These may due to the difference of the refuse components between Wuhan and other areas. In groundwater, 6 PAEs species were detected. According to the Surface Water Quality Criteria of China(GB3838-2002), the limit values of DEP, DBP and

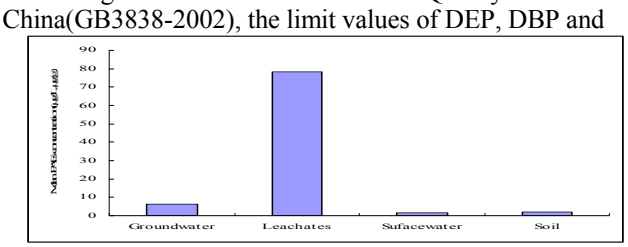

Figure 6. Comparison of mean PAEs concentrations in the four media

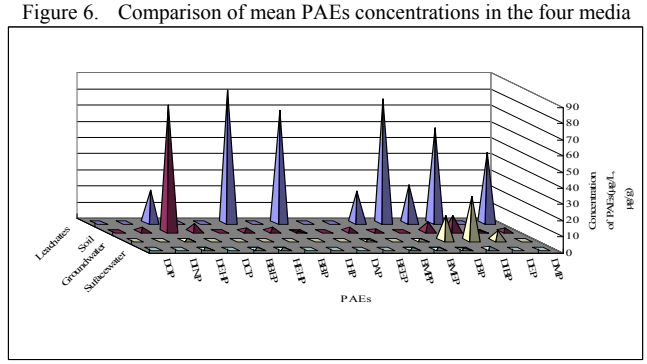

Figure 7. Distribution of individual PAEs in the four media from the MSW landfill (For the purpose of comparing the total PAEs concentratins of the four media, the contents in this figure is 10 times of the actual contents.)

DEHP for drinking water sources were 0.3, 0.003 and 0.008 mg/L, respectively. The concentrations of DBP in the groundwater of landfill area closed to the Quality Standard.

It's clear that the groundwater around the landfill was contaminated seriously and could not be served as the source of drinking water. Seven PAEs species were detected in surface water, and DBP, DIBP, and DEHP were present in [22-24]. In the soils, 12 PAEs were detected, and the major species were DIBP, DBP and DEHP.

ACKNOWLEDGMENT

This study was supported by the National Natural Science Foundation of China (Grant No. 40602038 and No. 40811120027).

REFERENCES

[1] C. A. Staples, D. R. Peterson, T. F. Parkerton, and W. J. Adams, "The environmental fate of phthalate esters: a literature review," Chemosphere, vol. 4, 1997, pp. 667-749.

[2] P. Serôdio, and J. M. F Nogueira, "Considerations on ultra-trace analysis of phthalates in drinking water," Water Research, vol. 40, Jul. 2006, pp. 2572-2582.

[3] S. Y. Yuan, C. Liu. C. S. Liao, and B. V. Chang, "Occurrence and microbial degradation of phthalate esters in Taiwan river sediments," Chemosphere, vol. 49, Dec. 2002, pp. 1295-1299.

[4] W. J. G. M. Peijnenburg, and J. Struijs, "Occurrence of phthalate esters in the environment of the Netherlands," Ecotoxicology and Environmental Safety, vol. 63, Feb. 2006, pp. 204-215.

[5] Z. Xie, R. Ebinghaus, C. Temme, R. Lohmann, A. Caba, and W. Ruck, "Occurrence and air-sea exchange of phthalates in the Arctic," Environmental Science and Technology, vol. 41, Jul. 2007, pp. 4555-4560.

[6] K. Kambia, T. Dine, B. Gressier, A. -F. Germe, M. Luyckx, C. Brunet, L.Michaud, and F.Gottrand. "High-performance liquid chromatographic method for the determination of di(2-ethylhexyl) phthalate in total parenteral nutrition and in plasma," Journal Chromatography B, vol. 755, Appl. 2001, pp. 297–303.

[7] K. M. Shea, and American Academy of Pediatrics Committee on Environmental Health, "Pediatric exposure and potential toxicity of phthalate plasticizers," Pediatrics, vol. 111, Jun. 2003, pp. 1467-1474.

[8] T. J. Wams. "Diethylhexylphthalate as an environmental contaminant —a review," The Science of The Total Environment, vol. 66, Oct. 1987, pp. 1-16.

[9] J. H. Richburg, and K. Boelkelheide. "Mono-(2-ethylhexyl) phthalate rapidly alters both sertoli cell vimentin filaments and germ cell apoptosis in young rat testes," Toxicology and Applied Pharmacology, vol. 137, Mar. 1996, pp. 42-50.

[10] E. Atlas, and C. S. Giam, "Global transport of organic pollutants: ambient concentrations in the remote marine atmosphere," Science, vol. 211, Jan. 1981, pp. 163– 165.

[11] H. H. Sung, W. Y. Kao, and Y. J. Su, "Effects and toxicity of phthalate esters to hemocytes of giant freshwater prawn, Macrobrachium rosenbergii," Aquatic Toxicology, vol. 64, Jun. 2003, pp. 25–37.

[12] P. G. Wu, G. G. Han, H. H. Wang, and Y. Zhao, "An investigation on Phthalates in drinking water. Journal of Environment and Health," vol. 16, 1999, pp. 338–339 (in Chinese).

[13] C. H. Mo, Q. Y. Cai, Q. T. Wu, B. G. Wang, H. Z. Huang, and L. X. Zhou. "A study of phthalic acid esters (PAEs) in the municipal sludges of China," China Environmental Science, vol. 21, 2001, pp. 362–366 (in Chinese).

[14] H. Gao, W. Y. Bao, and S. G. Zhang, et al.. Contaminative chemistry and ecotoxicology research, Yellow River Conservancy Press, Zhengzhou, China 2001, pp. 175 (in Chinese).

[15] D. S. Guo, X. Y. Yuan, Y. Yang, and X. J. Lv, "Water quality analysis to the water source of Wanjiazhai Yellow River water transfer project," Environmental Chemistry, vol. 21, 2002, pp. 271–275 (in Chinese).

[16] A. Coors, P. D. Jones, J. P. Giesy, and H. T. Ratte, "Removal of estrogenic activity from municipal waste landfill leachate assessed with a bioassay based on reporter gene expression," Environmental Science and Technology, vol. 37, 2003, pp. 3430-3434.

[17] J. D. Vilomet, A. Veron, J. P. Ambrosi, S. Moustier, J. Y. Bottero, and L. Chatelet-Snidaro, "Isotopic tracing of landfill leachates and pollutant lead mobility in soil and groundwater," Environmental Science and Technology, vol. 37, 2003, pp. 4586–4591.

[18] Y. H. Zhang, X. D. Chen, Z. S. Li, Z. H. Lei, and X. M. Liang, "Analysis of Phthalic Esters in lake sediments by GC/MS," Journal of Instrumental Analysis, vol. 14, 1995, pp. 17–21 (in Chinese).

[19] A. Yasuhara, H. Shiraishi, M. Nishikawa, T. Yamamoto, O. Nakasugi, T. Okumura, K. Kenmotsu, H. Fukui, M. Nagase, and Y. Kawagoshi, "Organic components in leachates from hazardous waste disposal sites," Waste Manage, vol. 17, 1999, pp. 186–197.

[20] H. Fromme, T. Küchler, T. Otto, K. Pilz, J. Müller, and A. Wenzel, "Occurrence of phthalates and bisphenol A and F in the environment," Water Research, vol. 36, 2002, pp. 1429-1438.

[21] H. Asakura, T. Matsuto, and N. Tanaka, "Behavior of endocrine-disrupting chemicals in leachate from MSW landfill sites in Japan," Waste Management, vol. 24, 2004, pp. 613–622.

[22] F. Zeng, K. Y. Cui, Z. Y. Xie, M. Liu, Y. J. Li, Y. J. Lin, Z. X. Zeng, and F.B. Li, "Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China," Environment International, vol. 34, 2008, pp. 372-380.

[23] Y. J. Sha, X. H. Xia, Z. F. Yang, and G. H. Huang, "Distribution of PAEs in the middle and lower reaches of the Yellow River, China", Original Article, vol. 124, 2007, pp. 277–287.

[24] F. Wang, X. H. Xia, and Y. J. Sha, "Distribution of Phthalic Acid Esters in Wuhan section of the Yangtze River, China," Journal of Hazardous Materials, vol. 154, 2008, pp. 317–324.

[25] X. H. Li, L. L. Ma, X. F. Liu, S. Fu, H. S. Cheng, and X. B. Xu, "Phthalate Ester pollution in urban soil of Beijing, People's Republic of China," Bulletin of Environmental Contamination and Toxicology, vol. 77, 2006, pp. 252-259.

[26] X. Y. Hu, B. Wen, and X. Q. Shan, "Survey of phthalate pollution in arable soils in China," Journal Environmental Monitoring, vol. 5, 2003, pp. 649-653.

[27] F. Zeng, K. Y. Cui, Z. Y. Xie, L. N. Wu, M. Liu, G. Q. Sun, Y. J. Li, D. L. Luo, and Z. X. Zeng, "Phthalate esters (PAEs): Emerging organic contaminants in agricultural soils in peri-urban areas around Guangzhou China," Environmental Pollution, 2008, in Press.