

## Occurrence and Concentration of Phthalate Esters in River Sediment Around Covenant Oxidation Ponds, Covenant University, Ota, Ogun State

Olujimi, O.O.<sup>1\*</sup>, Aroyeun, O.A.<sup>1</sup>, Akinhanmi, T.F.<sup>2</sup> and Arowolo, T.A.<sup>1</sup>

<sup>1</sup>Department of Environmental Management and Toxicology, Federal University of Agriculture, P.M.B. 2240, Alabata Road, Abeokuta, Ogun State, Nigeria

<sup>2</sup>Department of Chemistry, Federal University of Agriculture, P.M.B. 2240, Alabata Road, Abeokuta, Ogun State, Nigeria

### Abstract

Phthalate Esters (PEs) are well known environmental pollutants with wide application as plasticizers in plastic production. Concentrations of 8 PEs were determined in sediment samples collected from upstream and downstream of Covenant University Oxidation Pond (COP) between March and June 2013. Samples were extracted using the mechanical shaking method with double distilled dichloromethane. The prepared extracts were cleaned using activated silica gel-packed column chromatography and analyzed with high capillary gas chromatography equipped with flame ionization detector (GC-FID). The mean concentrations over the study period for the PEs, monoethylphthalate (MMP), dimethylphthalate (DMP), diallylphthalate (DAP), diethylphthalate (DEP), diisobutyl- (DIBP), di-n-butylphthalate (DBP), butylbenzylphthalate (BBP), and di-(2-ethyl)hexyl phthalate (DEHP) are 23.1 mgkg<sup>-1</sup>, 273 mgkg<sup>-1</sup>, 28.9 mgkg<sup>-1</sup>, 150 mgkg<sup>-1</sup>, 26.5 mgkg<sup>-1</sup>, 264.5 mgkg<sup>-1</sup>, 41.7 mgkg<sup>-1</sup>, and 20.9 mgkg<sup>-1</sup> for upstream samples. Mean concentrations for the downstream samples are 24.2 mgkg<sup>-1</sup>, 280 mgkg<sup>-1</sup>, 33.4 mgkg<sup>-1</sup>, 176 mg kg<sup>-1</sup>, 26.9 mgkg<sup>-1</sup>, 264 mgkg<sup>-1</sup>, 41.8 mgkg<sup>-1</sup>, and 18.2 mgkg<sup>-1</sup>, respectively. Generally, the PEs' concentration in downstream samples was significantly higher ( $p>0.05$ ) than upstream except for DIBP, BBP, and DBP whose DEHP concentrations were significantly higher ( $p>0.05$ ) upstream than downstream. The distribution pattern of PEs in the sediment is in the order DMP> DBP> DEP> BBP> DAP> DiBP> MMP> DEHP. The occurrence of PEs in the samples analyzed further supports their ubiquity in the environment.

**Keywords:** *Phthalate esters; sediment; oxidation pond; Nigeria*

### 1. Introduction

Phthalates or Phthalate Esters (PEs) are esters of phthalic acid and are mainly used as plasticizers to soften polyvinyl chloride (PVC) in order to increase their flexibility, transparency, durability, and longevity (Adewuyi., 2012; Alatrisme-Mondragon et al., 2003). PEs are readily soluble in

organic solvents (Hauser et al., 2004), and the longer their side chains, the higher their lipophilic tendency and boiling point (Mikula et al., 2005). PEs comprise a large group of compounds, several of them considered priority pollutants, e.g. dimethyl (DMP), diethyl (DEP), dibutyl (DBP),

\* Corresponding author: olujimio@funaab.edu.ng

butylbenzyl (BBP), di (2-ethylhexyl) (DEHP), and di-n-octyl phthalate (DnOP) (Swan et al., 2005). PEs are used in a large variety of products, such as outer covering of pharmaceutical pills, gels, dispersants, lubricants, binders, medical devices, waxes, detergents, textiles, children's toys, glues, inks, arms/ammunitions, and hairspray additives (Shanker et al., 1985; Kirkpatrick et al., 1989; Ling et al., 2007; Huang et al., 2008; Adewuyi and Olowu, 2012). They are also used in the production of adhesives, electronics, agricultural adjuvants, building materials, personal-care products, such as perfume, eye shadow, liquid soap and moisturizer, shower curtains, upholstery, surfactants, packaging, modeling clay, paints, printing inks, and coatings (Kayali et al., 2006; Huang et al., 2008; Adeniyi et al., 2008; Rudel and Perovich, 2009).

The main route of exposure to PEs is via water use, as these chemicals find their way into the water system through effluent discharges and leaching from waste dumps and several diffuse sources (WHO, 2003). PEs have been found to be ubiquitous in the environment and some of them have also been found to promote endocrine disrupting activities (Damstra et al., 2002; Williams et al., 2007). They are released into the environment through both direct and indirect means, and once in the environment, they are subject to biodegradation, photo-degradation, and anaerobic degradation. They do not persist in the outdoor environment. Outdoor concentrations are higher in urban and suburban areas than in rural and remote areas (Rudel and Perovich, 2009). The presence of PEs has been demonstrated in indoor dust (Hwang et al., 2008), food (Bosnir et al., 2007), rivers, sediments, lakes and seas, underground waters (Mihovec-Grdia et al., 2002), and wastewater (Yuan et al., 2002; Hashizume et al., 2002; Alatrisme-Mondragon et al., 2003; Adewuyi, 2012; Olujimi et al., 2012).

According to Mitsunobu and Takahashi (2006), sediment acted as sink for PEs due to their low values of aqueous solubility, volatility, and melting point. In addition, PEs tend to associate with sediment particulate material during the course of particle deposition in rivers and coastal waters due to their hydrophobic nature and high octanol/water partition coefficients (Staples et al., 1997). Sediments of smaller particle size and a larger surface volume with high organic carbon content

have the potential to accumulate significant concentrations of PEs (Rice et al., 1993). River sediments, therefore, are important sources for the assessment of anthropogenic contamination in surrounding environmental compartments, as they have a long residence time for organic pollutants like PEs (Heyden and New 2004). Several studies on the distribution and contamination level of PEs in sediments have been reported worldwide that reveal that polluted sediments are adversely affecting the ecosystem (Tan, 1995; Vitali et al., 1997; Fromme et al., 2002; Yuan et al., 2002; Peijnenburg and Struijs, 2006; Zeng et al., 2008). Therefore, in the present study, levels of PEs in sediment samples collected from upstream and downstream of receiving water bodies around COP have been investigated to assess the extent of contamination.

## 2. Materials and Methods

### 2.1 Reagents and Standards

The following phthalate standards were of analytical grade and were purchased from Supelco (Bellefonte, PA, USA): monomethylphthalate (MMP), Di-methylphthalate (DMP), Di-allylphthalate (DAP), Di-ethylphthalate (DEP), Diisobutylphthalate (DIBP), Di-n-butylphthalate (DBP), Butylbenzylphthalate (BBP), and DEHP (Di-(2-ethylhexyl) phthalate). Acetone, dichloromethane, and methanol were purchased from Sigma Aldrich (South Africa) and were further purified by double distillation at 70°C for 6 hours. The solvents were allowed to cool and were transferred into glass bottles and stored at room temperature prior to use. Anhydrous sodium sulphate was purified by heating in a muffle furnace at 450°C for 4 hours. Separate stock solutions of individual analytes were prepared in methanol (1000 mg l<sup>-1</sup>). A working mixture containing each compound at 10 mg l<sup>-1</sup> was also prepared and stored at 4 °C in the dark.

Silica gel used for the column chromatography was cleaned to prevent phthalate ester contamination. Briefly, 10 g of silica gel was weighed into a pre-cleaned glass thimble, inserted into the soxhlet, and extracted with double-distilled dichloromethane at 70°C for 8 hours. The silica gel was then transferred into pre-heated aluminum foil (250°C for 8 hours) and dried at 100°C for

16 hours in an oven. All the glassware that was used for sampling and sample preparation was initially washed with soapy water, rinsed with distilled water, and soaked in 10 % dil.  $\text{HNO}_3$  overnight. They were drained and rinsed with pre-double-distilled acetone and oven dried at  $250^\circ\text{C}$  for 8 hours. This is done to eliminate PE traces that are capable of contaminating samples.

## 2.2 Description of the Study Area

The Covenant University sewage treatment facility has four oxidation ponds and was constructed in 2002 when the university was established with the purpose of treating domestic wastewater generated within the school community. Wastewater is collected from hostels, school libraries, colleges, staff quarters, and other buildings within the school and channeled to the oxidation pond. However, water generated from the university cafeterias is not channeled to it. Oxidation and biological treatment (use of water hyacinth) are the processes used in the treatment of wastewater. The COP serves a population of about 6,000 people, and it releases its effluent into a river outside the university premises.

## 2.3 Sampling, Sample Preparation, and GC Conditions

Sediment samples were collected in triplicate upstream and downstream of the COP effluent discharge point. Samples were collected in glass containers with the aid of a glass scoop and stored in an ice chest immediately after collection and were later stored in the refrigerator at  $4^\circ\text{C}$  prior to extraction and analysis. Samples were defrosted and air dried in a semi-closed fume cupboard. Air-dried, homogenized, and sieved sediment was extracted using the method described by Olujimi et al. (2013). Ten grams of sediment was weighed into a 250 mL conical flask. Forty milliliters of dichloromethane was added, and the flask was covered with aluminum foil. The flask was shaken mechanically for 3 hours, after which, it was allowed to stand for 20 minutes. The extract was collected over a pre-extracted and oven-dried anhydrous sodium sulphate into a 250 mL round bottom flask. The mechanical shaking procedure was repeated twice, and the extract was combined together. The extract was dried in a fume cupboard by covering the round bottom flask with perforated aluminum foil. The dried extract was reconstituted with about 5 mL of dichloromethane prior to the

clean-up procedure. The procedure described above was adopted in preparation of blank samples for PEs determination. The GC-FID operating condition was used according to Olujimi et al. (2012). Briefly, oven inlet temperature was set at  $250^\circ\text{C}$ , carrier gas flow rate at  $1.0\text{ mL min}^{-1}$ , injector temperature of  $250^\circ\text{C}$ , split ratio of 50:1, the column used was HP 5MS, column dimension of HP-5MS (30 m x 0.32 mm x 0.25  $\mu\text{m}$ ), oven temperature was set at  $80^\circ\text{C}$  (1 min) ramped at  $5^\circ\text{C min}^{-1}$  to  $150^\circ\text{C}$  and held for 1 min, then to  $280^\circ\text{C}$  at  $12^\circ\text{C}$  (7 min), post run temperature was  $300^\circ\text{C}$  and held for 2 min.

## 2.4 Column Chromatographic Clean-up and Recovery Analysis

Pre-cleaned glass column was packed from bottom with 7 g of silica gel and 3 g of anhydrous sodium sulphate. The packed column was pre-conditioned using 20 mL of dichloromethane to remove trapped air and background contaminants within the column. The dichloromethane layer was maintained at 2 mm to prevent air infiltration into the column. The reconstituted extracts were quantitatively transferred into the column and eluted with 10 mL of dichloromethane. The eluted extracts were then air dried (as described above) to about 1 mL and quantitatively transferred using pasteur pipette into sample vials for GC-FID analysis. The method of Olujimi et al. (2013) was adopted for recovery analysis of sediment samples. Ten grams of sediment samples were spiked with 1 mL of  $10\text{ }\mu\text{g L}^{-1}$  of standard mixture of all PE congeners and air-dried for 15 minutes in an acetone, pre-cleaned fume cupboard. The samples were then extracted in triplicates using the mechanical shaking procedure described above. The effluent were air-dried and reconstituted with 5 mL of dichloromethane and cleaned on pre-treated silica gel as described above. The extracts were dried in a semi-closed- fume cupboard and reconstituted with dichloromethane and transferred quantitatively using pasteur pipette into sample vials for GC-FID analysis.

## 3. Results and Discussion

The recoveries obtained from the triplicate spiking experiments are presented in Table 1. The percentage recovery obtained varied from 76% (DEP) to 90.4% (DMP). The percentage recoveries

obtained in this study confirm the efficiency and acceptability of the analytical procedure described in this study. Studies on the blank samples gave a clean result as none of the PEs were detected in the blank determination for sediment.

**Table 1**

Recovery of PEs from Spiked Sediment Samples.

| PEs  | Spiked concentration in sediment. ( $\mu\text{gKg}^{-1}$ ) | Obtained concentration in sediment. ( $\mu\text{gKg}^{-1}$ ) | % Recovery |
|------|------------------------------------------------------------|--------------------------------------------------------------|------------|
| MMP  | 10                                                         | 8.42                                                         | 84.2       |
| DMP  | 10                                                         | 9.04                                                         | 90.4       |
| DAP  | 10                                                         | 7.96                                                         | 79.6       |
| DEP  | 10                                                         | 7.6                                                          | 76         |
| DIBP | 10                                                         | 8.38                                                         | 83.8       |
| DBP  | 10                                                         | 8.46                                                         | 84.6       |
| BBP  | 10                                                         | 8.04                                                         | 81.4       |
| DEHP | 10                                                         | 7.94                                                         | 79.4       |

The results of quantitative analyses of PEs in upstream and downstream sediment samples are

presented in Tables 2-4. Table 2 presents the concentration of PEs in sediments as well as the degrees of variation from one another, while the correlation levels of the PEs are shown in Table 3. All PEs analyzed were detected in all the samples.

For the month of March, the levels of phthalates in upstream samples ranged between  $20.1 \pm 0.12$  (MMP) and  $290 \pm 0.41$   $\mu\text{gKg}^{-1}$  (DMP), while downstream samples ranged from  $21.8 \pm 0.24$  (DEHP) to  $307 \pm 1.35$   $\mu\text{gKg}^{-1}$  (DMP). PE concentrations for April varied from  $23.5 \pm 0.15$  (DEHP) to  $265 \pm 1.06$   $\mu\text{gKg}^{-1}$  (DBP) for upstream samples and from  $16.7 \pm 0.22$  (DEHP) to  $290 \pm 1.84$   $\mu\text{gKg}^{-1}$  (DMP) for downstream samples. The concentrations recorded for the other months are presented in Table 2. MMP concentrations varied significantly ( $p > 0.05$ ) between upstream and downstream across the study period. There was no significant difference ( $p > 0.05$ ) between DMP concentrations upstream and downstream in June, while there was significant difference ( $p < 0.05$ ) between upstream and downstream for the other months under consideration.

**Table 2**

Concentration of PEs in Sediment Samples ( $\mu\text{gKg}^{-1}$ )

| PEs       | MMP               | DMP              | DAP                  | DEP              | DIBP              | DBP              | BBP                  | DEHP               |
|-----------|-------------------|------------------|----------------------|------------------|-------------------|------------------|----------------------|--------------------|
| MARCH UPS | $20.1 \pm 0.12^c$ | $290 \pm 0.41^d$ | $34.4 \pm 0.55^c$    | $161 \pm 0.04^e$ | $27.1 \pm 0.20^a$ | $266 \pm 0.56^a$ | $42.6 \pm 0.77^b$    | $23.05 \pm 0.30^f$ |
| MARCH DS  | $37.6 \pm 0.92^f$ | $307 \pm 1.35^e$ | $51.9 \pm 0.22^d$    | $214 \pm 1.49^g$ | $26.8 \pm 0.80^a$ | $263 \pm 1.25^a$ | $41.4 \pm 0.47^{ab}$ | $21.8 \pm 0.24^e$  |
| APRIL UPS | $33.4 \pm 0.57^e$ | $249 \pm 1.01^a$ | $36.1 \pm 0.17^c$    | $177 \pm 0.98^f$ | $27.2 \pm 0.17^a$ | $265 \pm 1.06^a$ | $41.7 \pm 0.27^{ab}$ | $23.5 \pm 0.15^f$  |
| APRIL DS  | $20.5 \pm 0.48^c$ | $290 \pm 1.84^d$ | $30.7 \pm 0.45^b$    | $157 \pm 0.06^d$ | $27.2 \pm 0.18^a$ | $264 \pm 0.37^a$ | $42.3 \pm 0.17^b$    | $16.7 \pm 0.22^a$  |
| MAY UPS   | $21.8 \pm 2.81^c$ | $286 \pm 4.88^d$ | $33.4 \pm 5.08^{bc}$ | $126 \pm 2.57^a$ | $26.4 \pm 1.58^a$ | $264 \pm 0.95^a$ | $41.6 \pm 0.54^{ab}$ | $17.4 \pm 0.31^b$  |
| MAY DS    | $26.9 \pm 1.46^d$ | $257 \pm 0.89^b$ | $14.6 \pm 0.41^a$    | $178 \pm 0.55^f$ | $26.5 \pm 1.31^a$ | $265 \pm 0.29^a$ | $41.6 \pm 0.56^{ab}$ | $16.4 \pm 0.31^a$  |
| JUNE UPS  | $17.0 \pm 3.17^b$ | $267 \pm 5.32^c$ | $11.7 \pm 0.25^a$    | $135 \pm 3.92^b$ | $25.1 \pm 3.88^a$ | $263 \pm 2.89^a$ | $40.8 \pm 1.43^a$    | $20.0 \pm 0.37^d$  |
| JUNE DS   | $11.8 \pm 1.01^a$ | $268 \pm 0.04^c$ | $36.5 \pm 0.53^c$    | $153 \pm 3.57^c$ | $27.2 \pm 0.17^a$ | $264 \pm 1.05^a$ | $42.0 \pm 0.11^{ab}$ | $17.9 \pm 0.26^c$  |

UPS- Upstream Sediment Sample, DS- Downstream Sediment Sample. Means with the same superscript column-wise are not significantly different.

**Table 3**

Mean Concentration of PEs in Sediment ( $\mu\text{gKg}^{-1}$ )

|          | MMP               | DMP              | DAP               | DEP            | DIBP             | DBP              | BBP                 | DEHP             |
|----------|-------------------|------------------|-------------------|----------------|------------------|------------------|---------------------|------------------|
| MEAN UPS | $23.1 \pm 7.16^a$ | $273 \pm 18.9^a$ | $28.9 \pm 11.5^a$ | $150 \pm 23^a$ | $26.5 \pm 0.9^a$ | $265 \pm 1^{ab}$ | $41.7 \pm 0.7^{ab}$ | $20.9 \pm 2.6^b$ |
| MEAN DS  | $24.2 \pm 10.7^b$ | $281 \pm 22^b$   | $33.4 \pm 15.4^b$ | $176 \pm 2^b$  | $26.9 \pm 0.3^a$ | $264 \pm 1^{ab}$ | $41.8 \pm 0.4^{ab}$ | $18.2 \pm 2.5^a$ |

UPS- Upstream Sediment Sample, DS- Downstream Sediment Sample. Means with the same superscript column-wise are not significantly different.

There was significant difference ( $p>0.05$ ) between upstream and downstream concentrations of DAP across the study period. DIBP and DBP concentrations did not vary significantly ( $p>0.05$ ) between upstream and downstream sediment samples across the study period. Table 3 shows the correlation levels of PEs as an indication of same source of occurrence into the matrix. MMP correlated with DAP and DEHP ( $p>0.01$ ) and with DEP ( $p>0.05$ ). DMP correlated with DAP ( $p>0.05$ ) but showed no relationship with other PEs. DAP showed correlation ( $p>0.01$ ) with DEP and DEHP only. However, DEP did not correlate with other PEs. DIBP correlated ( $p>0.05$ ) with DBP and BBP.

It was observed that mean PE concentration in sediment samples taken downstream was significantly higher ( $p>0.05$ ) than samples taken upstream for almost all the PEs except DIBP, BP, and BBP, which showed no significant difference ( $p>0.05$ ), while DEHP concentrations were significantly higher ( $p>0.05$ ) upstream than downstream (Table 4). With respect to this study, high concentration of all PEs confirms that sediment samples act as a “storage” or “reservoir” for phthalates (Mitsunobu and Takahashi, 2006; Fatoki et al., 2010). Low concentrations of DEHP were recorded in the sediment over the study period for the upstream and downstream samples.

The general distribution pattern for PEs in the sediment is in the order DMP> DBP> DEP> BBP> DAP> DIBP> MMP> DEHP. The distribution pattern reported in this study deviates totally from what has been reported in other countries, where DEHP usually accounted for higher concentration (Tan et al., 1995; Vitali et al., 1997; Fromme et al., 2002; Yuan et al., 2002; Peijnenburg and Struij, 2006; Zeng et al., 2008). Generally, the reported concentration of all the PEs except for DEHP are within the range reported in India, Germany, Taiwan, China, Netherlands, and Italy (Tan et al., 1995; Vitali et al., 1997; Fromme et al., 2002; Yuan et al., 2002; Peijnenburg and Struij, 2006; Zeng et al., 2008; Srivastava et al., 2010).

Olujimi et al. (2012) has reported similar changes in common distribution patterns of PEs in environmental matrices. However, the difference in distri-

bution patterns of this study compared to what has been reported elsewhere might be due to differences in PE congeners in the household products within the university communities.

**Table 4**

The Correlation of PE Sediment Samples

| Correlations |     |      |        |        |       |        |        |       |
|--------------|-----|------|--------|--------|-------|--------|--------|-------|
|              | MMP | DMP  | DAP    | DEP    | DIBP  | DBP    | BBP    | DEHP  |
| MMP          | 1   | .113 | .420*  | .772** | -.013 | -.173  | -.200  | .436* |
| DMP          |     | 1    | .572** | .197   | .142  | -.092  | .238   | .062  |
| DAP          |     |      | 1      | .511*  | .325  | -.067  | .266   | .414* |
| DEP          |     |      |        | 1      | .226  | .048   | .061   | .391  |
| DIBP         |     |      |        |        | 1     | .674** | .828** | .056  |
| DBP          |     |      |        |        |       | 1      | .731** | .088  |
| BBP          |     |      |        |        |       |        | 1      | .034  |
| DEHP         |     |      |        |        |       |        |        | 1     |

\*. Correlation is significant at the 0.05 level

\*\*. Correlation is highly significant at the 0.01 level

Correlation rating: >0.91= very strong; 0.91-0.81= strong; 0.81-0.31= moderate; <0.31=weak

## 4. Conclusion

The present study is a preliminary investigation and the first of its kind to assess the concentration and distribution of PEs around COP. The study reveals that PE congeners were present in all sediment samples analyzed. As expected, some PEs were more concentrated in downstream sediment. DIBP, DBP, and BBP showed no observable concentration difference, while DEHP was more concentrated upstream than downstream. This may be attributed to the release of untreated wastewater from the university cafeteria into this section of the river system. It is noteworthy to state that all obtained values are well under described environmental risk limits, which are 0.7 and 1mgkg<sup>-1</sup> for DBP and DEHP, respectively.

## Acknowledgement

Dr. Olujimi acknowledges IFS (Research Grant Agreement No. W/5065-1) for funding this study.

## References

- Adeniyi, A., Dayomi, M., Siebe, P. and Okedeyi, O. (2008), "An assessment of the levels of phthalate esters in the Muledane open dump, Thohoyandau, Limpopo Province, South Africa". Available at <http://journal.chemistrycentral.com/content/2/1/9>
- Adewuyi, G. O. (2012), "High Performance Liquid Chromatographic Identification and Estimation of Phthalates in Sewer Waste and a Receiving River in Ibadan City, Southwestern Nigeria", *Journal of Water Resource and Protection* 4: 851-858
- Adewuyi, G.O. and Olowu, R.A. (2012), "High Performance Liquid Chromatographic (HPLC) Method for Comparison of Levels of some Phthalate Esters in Children's Toys and Their Health Implications", *The Pacific Journal of Science and Technology* 13 (2):251-260
- Alatrisme-Mondragon, F., Iranpour, R. and Ahring, B. (2003), "Toxicity of di-(2-ethylhexyl) phthalate on the anaerobic digestion of wastewater sludge", *Water Research* 37: 1260-1269
- Bosnir, J., D. Puntaric, A. Galic, I. Skes, T. Dijanic, M. Klaric, M. Grgic, M. Curkovic, and Z. Smit. (2007), "Migration of Phthalates from Plastic Containers into Soft Drinks and Mineral Water", *Food Technology and Biotechnology*, 45(1): 91-95
- Damstra, T., Barlow, S., Bergman, A., Kavlock, R. J. and Van der Kraak, G. (2002), "Global assessment of the state-of-the-science of endocrine disruptors, WHO/PCS/EDC/02.2", *International Programme on Chemical Safety, World Health Organisation*, 1: 5-7
- Fatoki. O.S., Bornman. M., Ravandhalala. L., Chimuka. L., Genthe. B., Adeniyi. A. (2010), "Phthalate ester plasticizers in freshwater systems of Venda, South Africa and potential health effects", Available at <http://www.wrc.org.za>
- Fromme, H., Kuchler, T., Otto, T., Pilz, K., Muller, J., & Wenzel, A. (2002), "Occurrence of phthalates and Bisphenol A and F in the environment", *Water Research*, 36, 1429-1438
- Hashizume, K., Nanya, J., Toda, C., Yasui, T., Nagano, H. and Kojima, N. (2002), "Phthalate esters detected in various water samples and biodegradation of the phthalates by microbes isolated from river water", *Biological and Pharmaceutical Bulletins*, 25(2) 209-214
- Hauser, R., Duty, S., Godfrey-Bailey, L., and Calafat, A. M. (2004), "Medications as a source of human exposure to phthalates", *Environmental Health Perspectives*, 112(6): 751-753
- Health Organization. *Technical Report Series 778*. Geneva, Switzerland
- Heyden, C. J., and New, M. G. (2004), "Sediment chemistry: A history of mine contaminant remediation and an assessment of processes and pollution potential", *Journal of Geochemical Exploration*, 82, 35-57
- Huang, P.C., Tien, C.J., Sun, Y.M., Hsieh, C.Y. and Lee, C.C. (2008), "Occurrence of Phthalates in sediment and biota: Relationship to aquatic factors and the biota-sediment accumulation factor", *Chemosphere* 73: 539-544
- Hwang, H.M., Park, E.K., Young, T.M. and Hammock, B.D. (2008), "Occurrence of endocrine-disrupting chemicals in indoor dust", *Science of the Total Environment* 404:26-35
- Kayali, N., Tamayo, F.G. and Polo-Diez, L.M. (2006), "Determination of dimethylhexyl phthalate in water by solid phase microextraction coupled to high performance liquid chromatography", *Talanta* 69: 1095-1099
- Kirkpatrick, D. C., Ripley, R. A. and Pelletier, M. A. (1989), "Food packaging materials: health implications", *Nutritional Toxicology*, 3: 1-20
- Ling, W., Gui-Bin, C., Ya-Qi, H., Bin Ya-Wei, W. and Da-Zhong, S. (2007), "Cloud point extraction coupled with HPLC-UV for the determination of phthalate esters in environmental water samples", *Journal of Environmental Science* 19: 874-878
- Mihovec-Grđić, M., Šmit, Z., Puntarić, D. and Bošnjir, J. (2002), "Phthalates in Underground Waters of the Zagreb Area", *Croatian Medical Journal*, 43(4): 493-497

- Mikula P., Svobodová Z. and Smutná, M. (2005), "Phthalates: toxicology and food safety – a review", *Czech Journal for Food Science*, 23: 217–223
- Mitsunobu, S. and Takahashi, Y. (2006), "Study of the water solubility and sorption on particulate matters of phthalate in the presence of humic acid using  $^{14}\text{C}$  labeled di-(2-ethylhexyl) phthalate", *Water, Air and Soil Pollution*, 175, 99–115
- Olujimi, O.O., Fatoki, O.S., Daso, A.P., Akinsoji, O.S., Oputu, O.U., Oluwafemi, O.S. and Songca, S.P. (2013), "Levels of nonylphenol and Bisphenol A in wastewater treatment plant effluent, sewage sludge and leachates around Cape Town, South Africa", *Handbook of Wastewater Treatment*. ISBN: 978-1-62257-591-6
- Olujimi, O.O., Fatoki, O.S., Odendaal, J.P. and Daso, A.P. (2012), "Chemical monitoring and temporal variation in levels of endocrine disrupting chemicals (priority phenols and phthalate esters) from selected wastewater treatment plant and freshwater systems in Republic of South Africa", *Microchemical Journal*, 101: 11-23
- Peijnenburg, W. J. G. M. and Struijs, J. (2006), "Occurrence of phthalate esters in the environment of the Netherlands", *Ecotoxicology and Environmental Safety*, 63, 204-215
- Rice, D. W., Seltenrich, C. P., Spies, R. B, and Keller, M. L. (1993), "Seasonal and annual distribution of organic contaminants in marine sediments from Elkhorn slough, moss landing harbor and near shore Monterey Bay, California", *Environmental Pollution*, 82, 79–91
- Rudel, R. and Perovich, L. (2009), "Endocrine disrupting chemicals in indoor and outdoor air", *Atmospheric Environment*, 43 (1): 170–181
- Shanker, R.C., Ramakrishna, C. and Seth, P. (1985), "Degradation of some phthalic acid esters in soil", *Environmental Pollution*, 39:1-5
- Staples, C. A., Peterson, D. R., Parkerton, T. F. and Adams, W. J. (1997), "The environmental fate of phthalate esters: A literature review", *Chemosphere*, 35, 667–749
- Swan, S.H., Main, K.M., Liu, F., Stewart, S.L., Kruse, R.L., Calafat, A.M., Mao, C.S., Redmon, J.B., Tennant, C.L., Sullivan, S. and Teague, J.L. (2005), "Decrease in anogenital distance among male infants with prenatal phthalate exposure", *Environmental Health Perspective*, 113 (8): 1056–1061
- Tan, G. H. (1995), "Residue levels of phthalate esters in water and sediment samples from the Klang River basin", *Bulletin of Environmental Contamination and Toxicology*, 54, 71-176
- Vitali, M., Guidotti, M., Macilenti, G. and Cremisini, C. (1997), "Phthalate esters in freshwaters as markers of contamination sources—A site study in Italy", *Environment International*, 23, 337–347
- WHO (2003), Health Risks in Aquifer Recharged Using Reclaimed Water. Water Sanitation and Health. Protection and Human Environment. SDE/WSH/03.08. WHO, Geneva
- Williams, M., Woods, W., Kumar, A., Ying, G., Shareef, A, Karkkainen, M. and Kookana, R. (2007), "Endocrine Disrupting Chemicals in the Australian Riverine Environment: A pilot study on estrogenic compounds", [www.lwa.gov.au](http://www.lwa.gov.au). Accessed 2012-11-9
- Yuan, S.Y., Liu, C., Liao, C.S. and Chang, B.V. (2002), "Occurrence and microbial degradation of phthalate esters in Taiwan river sediments", *Chemosphere*, 49: 1295–1299
- Zeng, F., Cui, K., Xie, Z., Liu, M., Li, Y. and Lin, Y. (2008), "Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China", *Environment International*, 34, 372–380