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Phthalate Esters in the Environment: Sources and Quantification

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Abstract Consequent upon their widespread use as plasticizers and high volume of production, phthalates constantly diffuse and release into the various environmental components (air, water, soil) has become noticeable. In this study, levels and presence of phthalate esters were analyzed in newly purchased plastic toys and in polyethylene terphthalate (PET) bottled drinking water samples. Phthalate esters (PEs) in the samples were liquid-liquid extracted, pre-concentrated and analyzed for detection and quantification using HPLC. From the data obtained, the levels of DMP, DEP and DBP in the PET drinking water samples did not exceed the stipulated threshold levels while the level of DEHP was dominant and exceeded the safe limit. PEs were detected in all the 10 plastic toys samples analyzed including mouthable ones (teethers) used by children, imported into the country from China, Taiwan, etc . The values obtained revealed that the concentrations of PEs in the plastic toys ranged between 0.96 – 532 (µg/l). Also the percentage ($^{w}/_{w}$) values obtained were significantly higher and ranged between1.96 - 79.88% than the European Union (EU) recommended limits for all phthalate esters in toys, this portends risk to children who innocently put these toys in their mouth or chew them, as the toxic chemicals could leach into their blood stream. These results can be used as reference levels for future monitoring programs for pollution studies.

Keywords *PET* Drinking Water, Phthalate Esters, Plastic toys, Safety, Quantification

1. Introduction

Phthalate esters are the dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid (phthalic acid) produced by reacting phthalic anhydride with an appropriate alcohol (usually 6- to 13-carbon). They are colorless, odorless liquids with low water solubility, high oil solubility and low volatility (EPA, 2012). Phthalate esters are industrial chemicals used widely as plasticizers to impart flexibility and durability to polymers and plastics. Phthalates represent 69% of plasticizer used in USA, 92% in Western Europe and 81% in Japan [1].

Table 1 contains some of the 18 commercial phthalate esters. Phthalates are important industrial chemicals used in a variety of applications. These include pharmaceuticals (either as inactive ingredients in producing enteric coatings or as part of the active ingredients) and personal-care products (e.g. perfume, eye shadow, moisturizer, nail polish, liquid soap, hair spray), building/household materials (e.g. shower curtains, vinyl upholstery, adhesives, floor tiles), printing inks and coatings, food products (food and drink containers and wrappers) and textiles. Also included are adhesives, paints, insect repellant, detergent, packaging and production of children's toys and other children's products such as chewy teethers, soft figures and inflatable toys [2-3]. PET is suitable for food packaging applications, especially for drinking because of its chemical inertness and physical properties.

To provide flexibility, phthalates are not tightly bound to the plastic matrix, but are present as mobile components of the plastic matrix which leaches out of polyvinyl chloride (PVC) by surface contact with lypophilic substances especially when mechanical pressure is applied, therefore are easily released to the environment [4]. As plastics age and break down, the release of phthalates accelerates. Phthalate chemicals can be ingested, inhaled, or absorbed resulting in human exposure. The primary route of human phthalate exposure has been presumed to be ingestion, while the more volatile phthalates can be inhaled. Because phthalate plasticizers are not chemically bound to PVC, they can easily leach and evaporate into food or the atmosphere [5-6]. Phthalate exposure can be through direct use or by indirect means through leaching and general environmental contamination. Diet, especially fatty foods such as milk, butter, and meats is believed to be the main source of di-2-ethyl hexyl phthalate (DEHP) and other phthalates in the general population.

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Table 1. Names and Formular of Some Phthalate Esters

Name	Acronym	Abbreviation	CAS No.	Mol. Wt.
Diethyl phthalate	DEP	$C_6H_4(COOC_2H_5)_2$	84-66-2	222.2
Di-n-butyl phthalate	DBP	$C_6H_4[COO(CH_2)_3CH_3]_2$	84-74-2	278.3
Di(2-ethylhexyl) phthalate	DEHP	$C_6H_4[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]_2$	117-81-7	390.6
Dimethyl phthalate	DMP	$C_6H_4(COOCH_3)_2$	131-11-3	194.2
Diisononyl phthalate	DINP	$C_6H_4[COO(CH_2)_6CH(CH_3)_2]_2$	28553-12-0	418.60
Di-n-hexyl phthalate	DNHP	$C_6H_4[COO(CH_2)_5CH_3]_2$	84-75-3	334.5

Concern on the unusual ubiquity of phthalates in the environment has increased due to their wide range of toxicological characteristic [7]. Consequent upon their hydrophobicities, widespread use and high volume of production, phthalate constant diffuse and release into the various environmental compartment (air, water, soil) has become noticeable [8]. Phthalates are well recognized developmental and reproductive toxicants and have been implicated as endocrine disrupting chemicals based on recent epidemiological studies [9] with possible teratogenic and carcinogenic effects. DEPH and DBP are classified potential carcinogens, concluded as class B2 probable human carcinogens [10]. Body-care products containing phthalates are sources of exposure to infants and adults. The most widely used phthalates include DEHP, DIDP and DINP. DEHP is the dominant plasticizer used in PVC due to its low cost, DBP is used in epoxy resins as well as solvents in perfumes and personal care products while DMP and DEP are typically used in cellulose ester-based plastics and pesticides. In general, infants and toddlers are at the greatest risk of exposure, because of their mouthing behavior as they suck or chew on toys containing phthalates. DEHP is one of the most commonly used PEs as primary plasticizers in flexible vinyl products, such as soft teethers that may be mouthed by infants. Most children's toys are flexible plastics containing Poly Vinyl Chloride (PVC). The flexibility impacted by the PVC from the plasticizer (phthalates) ensures durability, softness, and ease of cleaning and of course, economical.

Consequently, several measures and regulations have been undertaken to reduce human exposure to phthalates [11]. To minimize the risk of food contamination with phthalates, specific rules and measures have also been set [12-13]. It has been established that toys are good sources of phthalate contamination in humans especially children (4 months to 4 years old) [14-15,4]. Strict means have been established with several measures and regulations been undertaken to reduce human exposure to phthalates by humans [16]. To this end, in the United States and Canada, the uncertainty in predicting exposure levels especially in very young children and infants, DEHP, DBP, BBP, DINP, DIDP and DnOP, have been prohibited to be used in children's toys such as infants' bottle nipples, pacifiers, teethers and infant toys intended for mouthing [17-18,14] at concentrations higher than 0.1% according to the Consumer Product Safety Improvement Act 2008 [19]. This study is aimed at assessment and quantification of 4 types of phthalates in children soft plastic toys as well as in PET drinking water samples.

2. Experimental

2.1. Samples Collection

Five (5) different brands of commonly sold and consumed bottled water from randomly selected Super markets in Wukari, Taraba Sate, Nigeria was used for this study. All the water samples were packed in PET plastic bottles with High Density polyethylene (HDPE) plastics. Also, ten (10) new plastic toys samples for children (5 months-4 years) such as Teethers, Barbie dolls, baby suckers, Plastic trucks and Rabbits were purchased from Supermarkets in Wukari Local Government area, Taraba State, Nigeria.

2.2. Quality Control and Assurance

Precautions were taken to avoid contaminations during sample collection and processing. It was ensured that no plastic equipment was used and all glasswares were precleaned. Also all equipments used were cleaned between samples and processing. All data were subjected to strict quality control procedures. Detergent was not used during sample processing. Quality assurance study was carried out in terms of Recovery Studies and Limit of Detection. The Recovery studies done for the PEs were carried out in order to ascertain the efficiency of extraction and analytical procedures adopted since there are no certified reference materials available. This was carried out by adopting the method stipulated by [20]. The Limit of Detection study carried out was to assess the lowest amount of analyte in sample; this was determined by adopting the method used by [21]. Identification was based on Retention time. Quantification of phthalate by internal standard was done by adopting the method of [21]. Analytical grade reagents of the PEs (DMP, DEP, DBP, DEHP) were purchased from Aldrich chemical company and Fluka AG, including the individual standard stock solution, and prepared in methanol.

2.3 Sample Pretreatment

About 1.0 L of each water sample for the PEs analysis was spiked with the PEs recovery standard then extracted by Liquid-liquid extraction in a separatory funnel using 3 x 50 ml dichloromethane for 7 h. The combined solvents extracted were dried over anhydrous sodium sulphate and concentrated using a rotatory evaporator. Plastic sections of the PVC toys were cuts into pieces and pulverized into plastic powder. 10 g of each pulverized powder were weighed using an analytical balance (Mettler Toledo AB250) and Liquid-liquid extracted with soxhlet extractor using 3 x 50 ml dichloromethane for 7 h at 60℃.

The combined solvents were dried in a glass chromatographic column (2.0 cm X 20 cm) packed with silica gel using anhydrous granular sodium sulphate. Hexane was used to elute the column for non-polar hydrocarbons and ethyl acetate was used to elute the column for phthalates prior to exposure to the Na_2SO_4 layer and concentrated in a thermostated water bath at 30℃. The residue was dissolved in 1 ml acetonitrile for instrumental analysis. Individual standard solutions of 100 mg/L of each of the phthalate standards and the internal standards were prepared by weighing accurately 1 mg of the standard into a 100 ml standard flask and made up to mark with the HPLC grade acetonitrile as solvent, from which standard mixtures of phthalates and internal standards were obtained. 20 µl of mixed standard solutions of the phthalates and the internal standards was added to the concentrated extract. The samples were transferred to a glass microvial for HPLC analysis.

2.4. Instrumental Analysis

An AKTA ^{tm} Basic 10/100 HPLC (Amersham Pharmacia Biotech) coupled with UV detector transmitting at 254 nm was used. It comprises a controller compartment, CU-900 monitor; UV-900 Pump; P-900 Valve (INV-907), an auto-sampler (A-900) with a flow cell of 10 mm with elution capacity 1.0ml/min at pressure of 10Mpa. Chromatographic separation was carried out using a thermostatic capillary column C_{18} (S_5OD52 250 cm X 3.0 mm) at ambient temperature. 20 µL was used as the injector volume and separation was performed under isocratic elution condition using acetonitrile and water (90:10) as mobile phase, under this condition the separation lasted for 12 mins.

2.5. Statistical Data Analysis

Samples with concentrations below the Limit of detection were assigned a value of zero for all concentration values. Field blanks and spiked blanks were used to determine any background contamination. The concentration values were corrected by the blanks data and statistical analysis were performed with Analysis Of Variance (ANOVA). The ANOVA was used for comparing the difference in the group mean concentrations of the PEs in samples for significance difference in the variance of the group mean concentrations.

3. Results and Discussion

3.1. PEs in PET Drinking Water Samples

The high values obtained for the percentage recovery studies of the PEs (57.48 - 89.00%) presented in Table 2 which compares favorably with that reported in literatures [20,22] gives credence to the efficiency of the analytical procedures adopted in the work. Values that ranged between 0.57 - 1.16µg/L obtained for the LOD demonstrated the high sensitivity of the analytical method adopted. The order of elution of the phthalates was DMP, DEP, DBP and DEH.

Among the four PEs investigated in the PET bottled water samples, DEHP was the most frequently detected (78.5%) followed by DBP (35.7%) (Table 3). In the study DEHP concentration ranged between 0.059 ±0.10 - 0.104 ±0.03 µg while the range 0.011±0.06 - 0.034±0.02µg l^{-1} was observed for DBP. DEP and DMP levels however, were below detection limit in all the PET-bottled water analyzed under this condition. The trend observed in this study for the detection patterns of the phthalates analyzed were in good agreement with those reported in several studies [23-25].

Table 2. Values of LOD, Percentage Recoveries, Retention Times and Retention Factor

PAEs	% Recoveries	Retention Factor	LOD (µg/L)	Retention Time (mins)
DMP	89.02	2.21	0.72	3.14
DEP	77.93	2.11	0.57	3.36
DBP	54.48	5.02	1.83	3.74
DEHP	83.50	1.77	1.16	4.27

Table 3. Mean Concentrations of (µg/g) PEs PET Drinking Water Samples (A1-A5)

PAEs	A1	A2	A3	A4	A5
DMP	ND	ND	ND	ND	ND
DEP	ND	ND	ND	ND	ND
DBP	0.034± 0.02	0.018± 0.02	0.026± 0.02	0.011± 0.06	0.026± 0.09
DEHP	0.059 ±0.10	0.104 ±0.03	0.078 ±0.05	0.084 ±0.04	0.062 ±0.07

3.2. PEs in Soft Toys

The values obtained for the Limit of Detection (LOD), Retention Time and Response Factor and Percentage Recovery of the PEs in the soft toys are recorded in Table 4. The trend of elution of the phthalates from the column was in the order of DMP, DEP, DBP and DEHP and their retention times are shown in Table 4. Values obtained for the LOD which is between 0.30-0.80 confirmed the high sensitivity of the analytical procedures adopted.

Table 4. Values of LOD, Percentage Recoveries, Retention Times and Retention Factors

Phthalates	Response Factor	% Recovery	LOD	R/T (Min)
DMP	1.41	12.83	0.70	3.13
DEP	1.29	74.70	0.80	3.33
DBP	3.41	25.77	0.30	3.71
DEHP	1.27	89.23	0.80	4.18

The present study was targeted at plasticized PVC toys (either wholly or partly of PVC) and so does not cover the entire range of toys on sales. The weight (%) of the phthalates in the plastic toys presented in Table 5, ranged between 1.96-79.88%. The results revealed that all inflatable toys (soft) were composed of phthalates plasticized PVCs (Table 5) and some at levels above the EU stipulated limit of 0.1% w/w in plastic toy [26]. Percentage by weight of DEHP and DBP detected were about 70% and 40% respectively, DEP (15%) and DMP (9.06%) were detected respectively in all the toys samples analyzed.

Table 5. Toy Types and Percentage (% w/w) Amount of PEs in Plastic Toy

Toy Types	DEHP	DEP	DMP	DBP	Total
Baby Sucker	35.89	5.06	3.39	27.54	79.88
Rabbit	10.38	2.92	1.54	1.22	16.06
Barbie Doll	ND	1.88	0.08	ND	1.96
Trucks	10.76	2.06	1.22	3.81	17.85
Teether	14.33	3.42	2.72	6.21	27.42
Total PEs	69.27	15.24	9.06	38.78	

The concentrations of the phthalates in the plastic toys samples shown in Table 6 ranged between 3.53 µg/L and 532 µg/L with DEHP being highest in Baby sucker. The order of prominence of the phthalates was in the order: DMP < DEP < DBP < DEHP. Phthalates levels in the toys were categorised into mouthable, soft squeeze and hard toys. It was observed that PEs concentrations in the hard toys (trucks and rabbit) were lowest. PEs levels was highest in the soft squeezable toys (baby sucker and Barbie doll and followed closely by teethers. The presence of PEs in the teether water samples is a pointer that phthalates are not bonded to the plastic matrix therefore liable to being leached out of the plastic matrix into the environment if the condition (pressure, temperature) for their movement is favoured. DMP, DEP and DPBP were determined in the blank sample for background contamination, thus confirming the ubiquitous nature of phthalates in the environment. Statistical analysis using ANOVA indicated that there was no significant difference between the group mean concentrations as F-value 0.51 (F cal) < 3.26 (F critical), that is, no significant difference between the variance of the samples of the soft mouthable toys and the hard toys. The Maximum Admissible Concentration (MAC) set by the US Environmental Protection Agency (EPA) for DEHP is 6 µg L [27] while the Threshold Limit Value (TLV) for DEP, DBP, DMP and DEHP were 0.55, 0.45, 5.0 and 5.0 mg L^{-1}, respectively.

Table 6. Mean Concentrations of Phthalate Esters in µg/g in toy samples and blank

Toy	DMP	DEP	DBP	DEHP
Blank	0.02±0.01	0.16±0.07	36±0.08	ND
Baby Sucker	134±2.04	91±0.08	376±5.57	532±1.14
Rabbit Carrot	ND	11±3.02	13±5.49	68±15.16
Barbie doll	ND	5±5.0	ND	ND
Trucks	18±11.19	8±5.2	24±6.4	54±0.71
Teether	43±0.02	64±0.06	104±0.28	243±6.4
Teether Water	3.53±0.1	ND	0.96±0.02	ND

4. Conclusions

From the results presented in this study, the following conclusions could be drawn: i. Two types of phthalates were detected in the PET bottled water samples sold in the area. DEHP was the highest detected phthalate followed by DBP, this could be based on extensive use of these two PEs industrially as well as their ubiquitous presence as environmental contaminants. ii. The concentrations of the detected phthalates were found to be significantly below the maximum levels established by FDA for bottled water (6 µg/L for DEHP in bottled water [28], iii. High significant levels of PEs in all children plastic toys samples analyzed for ages 4 months and 3 years. iv. Levels of PEs in soft toys is higher levels as compared to hard toys.

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