Phthalates in PET Bottles: Assessment of Human Exposure and Load to Landfills

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Abstract

Polyethylene terephthalate (PET) bottles have become an integral part of the packaged water industry, but their release of phthalate acid esters (PAEs) is a threat to human health and to the environment. The omnipresence of phthalates in the environmental compartments results in human exposure via multiple pathways such as dermal, oral and inhalation for prolonged periods. This study aims to investigate the phthalate presence in PET bottles and to assess the health risk of people working in landfills/recycling facilities being exposed to these pollutants through dermal contact.

MBP(1604 ng g^{-1}) was the most abundant compound detected in PET bottle samples, followed by MEP (1056 ng g^{-1}), DEP (413 ng g^{-1}), MiPP (216 ng g^{-1}), DnBP (189 ng g^{-1}), BBP (23.2 ng g^{-1}), MDHP (19.5 ng g^{-1}), DMiP (16.8 ng g^{-1}) and respectively. It is calculated that a total of 200.4, 131.96, 51.66, 23.66, 26.94, 2.443, 2.099 and 2.895 kg of MBP, MEP, DEP, DnBP, MiPP, MDHP, DMiP and BBP, respectively are disposed to the landfills/waste disposal sites through waste PET bottles. Mean concentration based dermal exposure estimated daily intake (EDI), target hazard quotient (THQ) and hazard index (HI) values were calculated. THQ values were determined as 0.007, 0.031, 0.113 for BBP, DEP and DnBP, respectively while HI (<1) indicated that the health risk was acceptable for all subjects. However, it is strongly recommended that regular monitoring of phthalates in PET on market shelves should be done to protect the health of consumers as well as to reduce pthalates loads to the environmental compartments.

Keywords: PET bottle, phthalate, environmental load, health risk assessment

1. INTRODUCTION

It is known that the bottled water industry has been in a continuous growth trend in recent years [1]. The general public perception is that bottled water is better than tap water for reasons such as taste, safety and portability [2, 3]. Polyethylene terephthalate (PET) bottles are the most widely used materials for packaging drinking water [4]. PET is a semi-crystalline polymer belonging to the family of polyesters [5]. It is synthesized as a result of the reaction of ethylene glycol ($C_2H_6O_2$) catalyzed by antimony oxide, with terephthalic acid or its methyl ester [6]. The plastics industry generally claims that PET bottles are not a

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source of endocrine disruptors [7]. However, studies have shown that some plasticizer chemicals with endocrine activity are found in water stored in PET bottles in varying proportions depending on storage conditions [8]. Plasticizer; defined as "A substance incorporated into a plastic or elastomer to increase its flexibility, machinability, or stretchability." by ASTM [9] [10]. Briefly, plasticizer; It is an organic solvent with a high boiling point that gives it flexibility when added to a solid.

Phthalates are a group of industrial chemicals with wide commercial use as plasticizers [11]. Plastic bottles made of PVC or polyethylene are widely used in many countries to store drinking and tap water. PET bottles are the most used because of their physical and chemical tolerance [12]. Although phthalates are not allowed to be used in the manufacture of food contact materials as of 14 January 2011 by the European Commission's regulation 10/2011, phthalates have been detected in PET materials and in water stored in PET bottles [13]. Possible reasons for this situation; The quality of the raw material and the technology used in bottle production or the chemicals used in the production process, the use of recycled PET, the contamination of water sources with plastic waste, cross-contamination by phthalates present in the environment during bottling, and contamination from cap seals [4]. Phthalates can be divided into two groups according to their molecular weight. Low molecular weight phthalates (ester side chain lengths 1-4 carbons); dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-n-butyl phthalate (DnBP) are commonly found in personal care products (perfume, shampoo and nail polish) to balance color and odor. High molecular weight phthalates (ester side chain lengths, five or more carbons); di-(2-ethylhexyl) phthalate (DEHP), di-octyl phthalate (DOP), and di-isononyl phthalate (DINP) are used in plastic pipes, food packaging and processing materials, and many PVC products [14]. Phthalates are generally lipophilic, which affects their percolation and diffusion properties [15]. Phthalates used as plasticizers in polymers are not chemically bound to the polymers. For this reason, they have the potential to pollute the environment by easily migrating from polymers or separating as gas. Humans are also exposed to high concentrations of these compounds, especially when products containing phthalates are exposed to high temperatures [11, 16]. Phthalates are not covalently bonded in the plastic matrix. Because; they migrate to food and other materials or become airborne [17]. The leaching of traces of phthalate esters (PAEs) from PET bottles and their effects on human health has become a serious concern. Phthalates have been detected in the atmosphere [18], aquatic environments [19, 20], and food and beverages [21] [6]. These compounds, which are called Endocrine-Disrupting Chemicals (EDCs) due to their hormonal activity, pose a serious danger to health.

The United States Environmental Protection Agency (USEPA) has added phthalate esters to the list of "chemicals of concern" due to the health risks it poses [22]. DEHP, DBP, BBP, DIBP, DINP, DIDP, DNOP have been classified as carcinogenic, mutagenic or toxic to reproduction (CMR) of category 1B by the European Chemical Agency (ECHA). This classification is made between 4 and 1, and 1 is considered as the most dangerous group. Considering this situation, legal regulations are made in food contact materials [23]. According to the regulation numbered 10/2011 accepted by the European Union (EU) Commission, the limit values of DEHP, BBP and DBP concentrations allowed in food contact packaging material were determined as 1.5, 30 and 0.3 mg/kg, respectively [24]. In our country, the use of phthalate esters in food contact packaging material is limited by the Turkish Food Codex [25]. The Turkish Food Codex complies with the European Union (EU) legal regulations.

Although there are very limited studies [26-28] in Turkey on the level of phthalate in packaged drinking water, which we use a lot in our daily lives, the level in PET bottles has not been examined yet. Phthalate levels in PET bottles have also been limitedly studied worldwide [13]. Since phthalates used as plasticizers in PET products do not form covalent bonds with polymers, they can be separated from the structure of the plastic and released into the environment. To investigate the presence of this effect, PET bottles of 16 different bottled water companies sold currently in supermarkets in Bursa province were analyzed and phthalate concentrations (25 different PAEs) were determined. In this manner, the main goals of this study were: (1) to determine levels of phthalates (Bis(2-ethylhexyl) phthalate (DEHP), Diallyl phthalate (DALP), Diamyl phthalate (DAMP), Dicyclohexyl phthalate (DCHP), Diethyl phthalate (DEP), Dihexyl phthalate(DHP), Diisohexyl phthalate(DiHP), Diisopentyl phthalate (DiPP), Dimethyl isophthalate (DMiP), Dimethyl phthalate (DMP), Di-n-butyl phthalate (DnBP), Diphenyl phthalate (DPP), Isobutyl Cyclohexyl Phthalate (iBCHP), Monoisopropyl phthalate (MiPP), Mono-2-heptyl phthalate (MDHP), Monobenzyl phthalate (MBEP), Monobutyl phthalate (MBP), Monocyclohexyl phthalate (MCHP), Monoethyl phthalate (MEP), Monoethylhexyl phthalate (MEHP), Monohexyl Phthalate (MHP), Monoisononyl phthalate (MiNP), Monomethyl Phthalate (MMP), Mono-n-pentyl phthalate (MnPP) and Monooctyl phthalate (MOP)) in PET bottle samples collected in supermarkets in Bursa (Turkey), (2) to determine phthalate uptake rates for people working in landfill areas via dermal contact to the PET bottles; (3) to estimate the annual amount of phthalates released to landfills.

2. MATERIALS and METHODS

2.1. Collection of Samples

A total of 16 PET bottles were purchased from various markets in Bursa (Turkey). Information including bottle weight and bottle dimensions of the analyzed PET bottles were recorded.

2.2. Chemical Reagents

The compounds of DEHP, DALP, DAMP, DCHP, DEP, DHP, DiHP, DiPP, DMiP, DMP, DnBP, DPP, iBCHP, MiPP, MDHP, MBEP, MBP, MCHP, MEP, MEHP, MHP, MiNP, MMP, MnPP and MOP were purchased from Accustandard (New haven, CT, USA). High purity organic solvents were of HPLC grade while solid chemicals were ACS grade.

2.3. Measurement of phthalates in PET Bottle samples

PET bottle samples taken from the markets were emptied, rinsed with ultrapure water and dried. Bottles were cut into 0.5 cm circles, followed by analysis of PAEs contents according to the National Standard Methods for the Analysis of PAEs (GB/T21928-2008, China). Briefly, 0.3 gr PET bottle piece was treated 20 ml of hexane, 5 ml of acetone and recovery solutions (d4- dimethyl phthalate (DMP-d_4), d4- diethyl phthalate(DEP-d_4), d4- dicyclohexyl phthalate (DCHP-d_4), d4- bis(2-ethylhexyl) phthalate (DEHP-d_4) and d16- bisphenol A (BPA-d_{16}) under ultrasonic extraction for 30 min. After filtration, this process was repeated on residual plastic two more times with 5 ml of hexane (HEX) and 1 ml of acetone (ACE). The three batches of aliquots were pooled, transferred to a glass bottle, and dried by rotary evaporation. The dried sample was transferred to the GC vial and dissolved in 1 ml of methanol (MeOH):ACE (1:1) for PAE analysis and internal standard (d4-isobutyl phthalate) was added.

2.4. Instrumental Analysis

Analysis of targeted chemicals were performed using a Shimadzu 8040 triple quadrupole LC-MS/MS system and separation was achieved on a Shim-pack FC-ODS (150 x 2 mm, Shimadzu, Kyoto/Japan) column. Mobile phase was composed of 10 mM ammonium acetate in water (A) and Acetonitrile (B). The solvent gradient was as follows: 0.0–1.0 min; 80% of solvent B, 1.0–2 min; a linear gradient to 95% of solvent A; 2.0-4.0 min 95% solvent B; 4.0-4.01 min gradient to 50% solvent B; 5.0 min stop. Injection volume was 10 µL and the column flow rate and oven temperature were set 0.3 mL/min and 40 ℃, respectively. The capillary voltage was kept with 4.0 kV, and vaporizer temperature was 350 ℃.

2.5. Statistical Data Analysis

SPSS Statistics 26 (IBM) was used for statistical analyses. Data were expressed as mean ± standard deviation (SD) and SD was greater than 20% of the mean value across all data. A standard deviation that is very close to or higher than the mean indicates a highly heterogeneous distribution of the data.

2.6. Health Risk Assessment

Eq. (1) and (2) were used to calculate the dermal contact exposure assessment of the people working there with the disposal of PET bottles to landfills. Estimated daily intake by dermal contact (EDI): Estimated daily intake of phthalates (mg/kg/day BW) by dermal contact with PET bottles was calculated using the Eq. (1)[29, 30]:

$$\mathrm{EDI} = C_{total} \times \mathrm{SA} \times \mathrm{P} \times \mathrm{ED/BW} \quad (1)$$

where EDI is the dermal exposure dose (mg (kg d)$^{-1}$); C_{total} is total phthalate concentration (mg/kg); ED is exposure duration (9 h d^{-1}), which was determined by daily working hours per individual including break times; SA is the dermal exposure area (0.08 m^2), including the area of hands [29, 30]. P is the overall skin permeability coefficient for pollutants (5.8 m h^{-1})[31]; BW is body weight (70 kg) [32].

Target Hazard Coefficient (THQ): Used to calculate the non-carcinogenic risk of exposure to heavy metals. The hazard ratio of a single pollutant is determined by the Eq. (2)[33]:

$$THQ = \frac{EDI}{RfD} \quad (2)$$

where, THQ is the target hazard coefficient, EDI is exposure dose (mg/kg/day), RFD is oral reference dose (0.2 mg/kg/day for BBP, 0.8 mg/kg/day for DEP, 0.1 mg/kg/day for DnBP)[33].

3. RESULTS AND DISCUSSION

3.1. Phthalate Concentration in PET Bottle Samples

Mean and median concentrations of phthalates detected in PET bottles are shown in Figure 1 and descriptive statistics of phthalates were summarized in Table 1. MBP showed the highest concentration with a mean concentration of 1604±1238 ng g^{-1}, whereas the lowest concentration was measured for DMiP (16.8±21.0 ng g^{-1}) (Fig. 1). The mean concentrations of the phthalates were found in the order MBP(1604±1238 ng g^{-1}) >MEP (1056±1749 ng g^{-1}) >DEP (413±510 ng g^{-1}) >MiPP (216±231 ng g^{-1}>DnBP (189±156 ng g^{-1}) >BBP (23.2±7.15 ng g^{-1}) >MDHP (19.5±21.5 ng g^{-1}) >DMiP (16.8±21.0 ng g^{-1}) (Table 1). Other phthalates were not present in analysed samples. In a study conducted in Beijing/ China, concentration levels in PET bottles were 22.88-182.43 ng g^{-1} for DEP, 9.07-188.58 ng g^{-1} for DMP, and 62.90-511.52 ng g^{-1} for DBP [13]. However, BBP, di-n-octyl phthalate (DOP) and DEHP were not detected [13]. These results were different from our study for PET bottles, in which only DEP was detected at concentrations ranging from 114 to 2108 ng g^{-1}. A considerable variation in the concentrations of phthalates, especially MBP, MEP found in various PET bottle samples can be inferred from the standard deviations in Figure 1. According to Turkish Food Codex, the limit values of DEP, DBP, BBP, DEHP, DiDP and DiNP concentrations allowed in food contact packaging material were determined as 12, 0.3, 30, 1.5, 9 and 9 mg/kg, respectively [25]. In this study, only DEP and BBP were found in the analyzed samples and they did not exceed the limit values.

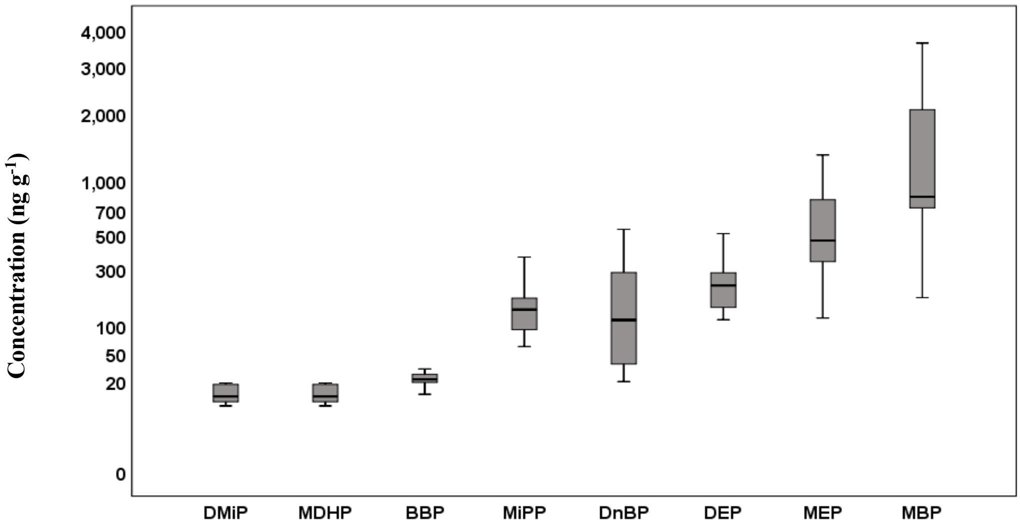

Figure 1. Phthalate levels measured in the PET bottle samples (The top and bottom ends of the box represents the 75th and 25th percentiles of the data set, respectively. The extensions ("whiskers") at either end of the box indicate the maximum and minimum values. The median concentrations are indicated by the horizontal line in the boxes)

Table 1. Descriptive statistics

	BBP	DEP	DMiP	DnBP	MiPP	MDHP	MBP	MEP
Mean	23.2	413	16.8	189	216	19.5	1604	1056
Median	22.5	217	10.6	181	142	10.9	1161	507
Std. Deviation	7.15	510	21.0	156	231	21.5	1238	1749
Skewness	0.662	2.82	2.45	0.776	2.66	2.46	0.946	3.68
Std. Error of Skewness	0.564	0.564	0.564	0.580	0.564	0.597	0.564	0.564
Kurtosis	0.591	8.63	6.05	0.041	7.76	5.77	-0.033	14.16
Std. Error of Kurtosis	1.09	1.09	1.09	1.12	1.09	1.15	1.09	1.09
Minimum	12.1	114	0.00	19.9	59.8	6.56	180	119
Maximum	39.9	2108	81.3	542	967	82.3	4336	7454

3.2. The Amount of Phthalates Disposed to the Landfills/Waste Disposal Sites

Reports states that 165000 tons of PET bottles are produced annually in Turkey. However, only 40000 tons of this is subjected to recycling. Consequently, it is estimated that approx. 125000 tons of PET bottles are thrown into nature and landfills every year[34]. Based on the concentrations we detected in PET samples, it is calculated that a total of 200.4, 131.96, 51.66, 23.66, 26.94, 2,443, 2.099 and 2.895 kg for MBP, MEP, DEP, DnBP, MiPP, MDHP, DMiP and BBP, respectively are disposed to the landfills. The annual amount of phthalates disposed to the landfills/waste disposal sites is presented in Fig. 2.

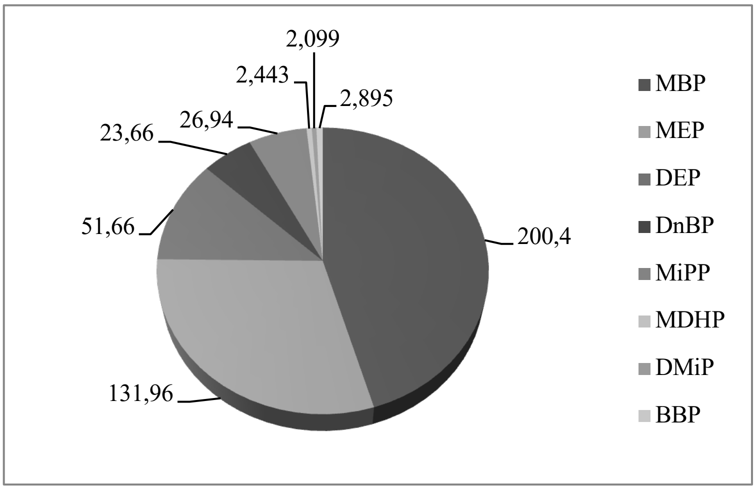

Figure 2. The annual amount of phthalates disposed to the landfills

3.3. Risk Assessment

Health risk assessment of PAEs for people working in recycling facilities and landfill areas shown in Table 2. The mean concentrations of pthalates in PET bottles were used to calculate the estimated daily intake (DE), target hazard quotient (THQ) and hazard index (HI) associated with dermal exposure of waste recycling industry workers to these chemicals. THQ values were determined as 0.007, 0.031, 0.113 for BBP, DEP and DnBP, respectively. HI (0,161) indicated that the health risk was acceptable for all subjects (HI <1), but regular monitoring of phthalates in PET on market shelves should be done to protect the health of consumers as well as to reduce pthalates loads to the environmental compartments.

Table 2. Health risk assessment of PAEs for people working in recycling facilities and landfill areas

	BBP	**DEP**	**DnBP**	**DMiP**	**MiPP**	**MDHP**	**MBP**	**MEP**
DE (mg (kg day)$^{-1}$)	0.001	0.025	0.011	0.001	0.013	0.001	0.096	0.063
THQ	0.007	0.031	0.113	nc	nc	nc	nc	nc

nc: not calculated as RFD values is not available in the literature

4. CONCLUSION

PAEs including BBP, DEP, DMiP, DnBP, MiPP, MDHP, MBP and MEP were detected in PET bottles. Research has shown that plastic bottles are a source of PAEs in landfills and more stringent measurements are needed to reduce the potential health risk of PAEs in PET bottles. Importantly, the release of PAEs from PET bottles into the environment could be delayed by taking various precautions (avoiding high temperatures, long storage time and UV radiation) during storage. As expected, the concentrations of PAEs in PET bottles were negligible for consumers. Of course, more research is needed to assess the potential risk to human health due to direct and indirect human exposure via different pathways, including water, food and air.

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