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Health Risk Assessment of PET Bottles in GCC

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***Abstract*—**Bottle water is getting very popular all through the world; especially in the gulf countries as the main source of drinking water. However, concerns over leaching of toxic chemicals are increasing. In this study, a health risk assessment was conducted in accordance with the guidelines indicated by United States Environmental Protection Agency *(*USEPA). It is conducted based on leaching of Diethyl Phthalate (DEP) from Polyethylene terephthalate (PET). The toxicity and exposure assessment of diethyl phthalate was conducted to characterize its risk on human health. Risk management is also discussed.

***Keywords*—**Toxicity, diethyl phthalate, PET, risk Assessment.

I. Introduction

WITH the increase in the diversification of human activities as well as the rapid advancement in technological resources, a broad range of chemical products and compounds have infiltrated the ecological system. In order to protect the public health, risk assessments are needed to investigate the different factors affecting risk to particular compounds and products.

Plastic water bottles are essential part of our society. It is easy to carry and portable enough to be stored in a small area. Due to its size and strength, plastic bottles are very popular in our modern age. There are different types of plastic that are being used to make plastic water bottles [1-2]. Polyethylene terephthalate (PET) is what most water bottles are made of and this type of plastic is intended to be disposed because reuse can cause bacteria to grow [3]. PET bottles are known to leach different types of chemicals (i.e. phthalate, antimony and similar compounds), even though PET producer companies denied it over the years [4-5].

Arab Countries involved in Gulf Cooperation Countries (GCC) are heavily dependent on PET bottle waters as their main source of water for drinking [6]. Although many of the water utilities supply good quality desalinated water, culturally these countries use bottle water as their main source of water consumption. It increases the risk associated with exposure to contaminants leached from these bottles. It is essential to investigate the health risk imposed by over dependency of these types of bottles.

The objective of this study was to investigate human health risk assessment caused by Diethyl Phthalate (DEP) leached from PET water bottles. The risk assessments were conducted based on the procedures suggested by the United States Environmental Protection Agency (USEPA) (Fig. 1). In this Risk Assessment (RA), the risk associated with the human intake of a certain type of Phthalate is assessed. Toxicity and exposure assessments were done to assess risks and toxicity levels upon human health. Probable risk management suggestions were also made.

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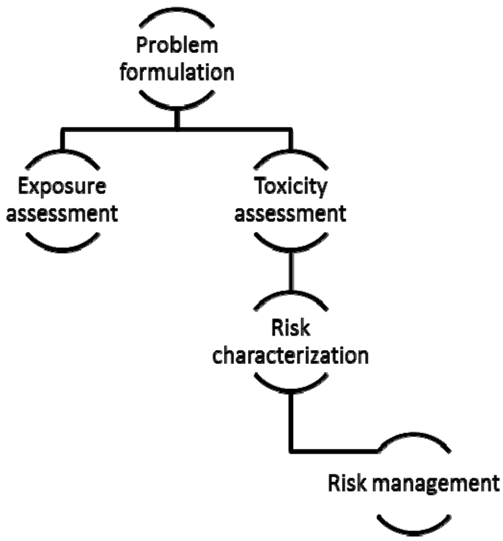

Fig. 1 Model of Human Health Risk Assessment

II. Assessment of the Problems

A. Definition of the Problem

In recent years, extensive environmental research has been conducted upon the effects of phthalates on health as some studies have confirmed that human exposure to these chemical compounds results in health impacts [7-10]. Phthalates are subcategorized in several components according to their chemical bonding and structural organization. Moreover, this assessment will focus upon a single component, which is the Diethyl Phthalate. Since Diethyl Phthalate is one of the emerging contaminants, there is few or scarce research done relating to this component and hence risk assessments conducted were not conducted. Since the health impacts and risks associated with this compound are relatively unclear, this health risk assessment was focused upon clarifying the health impacts and the risk parameters associated with Diethyl Phthalate.

Definition of the Regulatory Action

Currently, several organizations regulate the human exposure to the Diethyl Phthalate. United States Environmental Protection Agency (USEPA) designates DEP as a toxic pollutant 307(1) (a) of the Federal Clean Water Act and it is subject to effluent guidelines [11]. In addition to that, USEPA assigned Dimethyl Phthalate a weight-of-evidence carcinogenic classification of D, which translates that DEP is not a carcinogenic compound.

B. Diethyle Phthalate in PET Water Bottle

PET water bottles are made through polycondensation of purified terephthalic acid (PTA) with ethylene glycol [12]. PET is widely used due to its resistance to temperature fluctuation, transparency, chemical resistance and abrasion proof. Majority (60%) of the PET produced in the world are for synthetic fibers. Bottle production accounts for around 30% of the global demand [13]. PET can be subjected to various types of degradations, leading to potentially leaching of different chemicals.

III. Analysis

A. Toxicity Assessment

PET bottles can leach different chemicals. Acetaldehyde, antimony, phthalates are some of the chemicals suspected of leaching from PET [4-5, 14]. Phthalates are used as plasticizers in the production of PET bottles. Diethyl phthalate ($C_{12}H_{14}O_4$ DEP) is one of the most important phthalates (around 30% of the total phthalate) that can leach from PET bottles. DEP has different adverse effects on living organisms. The severity of adverse health effects associated with DEP depends on the significance of exposure level by the living organisms, the route and the period of exposure.

The different levels of DEP consumption can result in different health effects; those effects include death, immunological, developmental, neurological, carcinogenic, and other effects. In this paper, the different types of health effects of oral exposure to Diethyl phthalate will be examined.

According to a study done on rabbits and guinea pigs, the lowest dose of diethyl that had lethal effects was found to be 4,000 and 5,000 mg/kg, respectively [1].

Moreover, experiments had shown that oral exposure of rats to DEP had cardiovascular effects [15]. The heart weight of the rats had shown a significant increase due to an oral exposure to a dosage of 3,160 mg/kg/day of DEP. In addition to that some gastrointestinal effects had been observed after a two-to-16-week oral exposure DEP with high concentrations. This exposure enlarged the stomachs, resulted in small intestines and caucus in some cases.

Several hematological effects had also been apparent on animals after oral exposure to DEP [15]. An experiment on male rats had shown an increase in erythrocyte counts after receiving 3,160 mg/kg/day which makes 5% of the diet for 6 weeks. Nevertheless, that resulting increase had disappeared in a time period of 16 weeks.

Furthermore, several experiments had shown that DEP had several Hepatic Effects on the experimental rats [15-16]. An increase in liver weights has been observed on the animals that had been fed with 3,710 mg/kg/day dose of diethyl phthalate for duration of 14 days and less.

Besides, some animals that were orally exposed to diethyl phthalate for 16 weeks showed Fatty degeneration. It was also observed that adding a dose of 250-1,000 mg/kg/day diethyl phthalate to the food of guinea pigs for 1-3 months has caused congestion, scant, and cloudy swelling [1].

The experiments examining the renal effects of diethyl phthalate on rats have shown that injecting the food of the rats with 5% diethyl phthalate which is equivalent to 3,160 mg/kg/day for two weeks had shown an increase in the relative weight of the kidney. This change in weights was not proved to cause any functional damages. Since there had been no evidence of any damages caused to the kidney it was inferred that the increase in the weight of the kidney was most likely not a result of a toxic effect of the DEP.

Most of the phthalic esters have been found to have toxic effects on the reproductive system of the male. As a result, a number of studies have investigated the effects of DEP on the reproductive system of the male rat [17]. The dose that was found to have serious effects on reproductive system of a male rat was determined to be 3250 mg/kg/day [18].

Due to the variation of concentration of DEP that was being exposed to, in a dose-dependent toxicity study of DEP, it was found out that exposure to DEP for long periods of time and at low concentrations for longer period results in an increase in liver to body weight ratio in the rats [19].

In general, Cholesterol and Glycogen are produced as well as destroyed in the liver and exposure to increasing concentrations of DEP causes an elevated accumulation of cholesterol and glycogen in the liver in a dose-dependent manner.

B. Exposure Assessment

There are different routes of exposure to DEP that can be examined in order to study its adverse effects, those routs include inhalation, oral, and dermal exposure. DEP could be exposed through numerous pathways as it could be found in soil, water, plastics, insect repellents and air. The exposure could happen through inhaling contaminated air or drinking contaminated water, eating contaminated food or even through the skin.

The exposure of DEP could happen also indirectly, for instance, during certain manufacturing activities or disposal of products which might contain DEP products. DEP levels have been measured at different locations and different events and Table I identifies the level of concentration in each case [20]. Plastic packaging, soil and surface water bodies appeared to have the highest amount of DEP presence.

TABLE I
CONCENTRATION OF DEP AT DIFFERENT LOCATIONS [20]

Location	Diethyl Phthalate Concentration (ppm)
Hazardous waste sites in the ground water	0.0125
Hazardous waste sites in surface water	0.0121
Soil	0.039
Drinking water	0.00001-0.0046
Industrial waste water	0.00001-0.060
River water	0.00006-0.0044
Sediments from large water bodies	Up to 0.042
Indoor air	0.00018-0.00022
Outdoor air	0.00004-0.00006
Plastic Packaging (for food storage)	2-5

Based on the daily food intake of an average human, consumption of DEP is found to be four milligrams. On the other hand, if a person is exposed annually to contaminated water then his or her annual exposure of diethyl phthalate would be 0.0058 milligram per year. The duration of exposure to the DEP often plays an important role on its impacts on humans. It is difficult to find studies that would show the direct impact of such contaminants on humans. However animals could substitute, an experiment was conducted on rats in order to investigate the intermediate-duration exposure [19]. After sixteen weeks, the rats started to lose weight and their food consumption started to decrease. This problem is considered a long term effect. Unless the rats were exposed to very high doses, DEP would not lead to death. However, till today there is no carcinogenicity or chronic studies that describe the impact of exposing DEP through oral, inhalation or dermal exposure.

The leaching or organic compounds are thought to pose risk to the health of consumers. Atmospheric conditions such as high temperature and sun radiation facilitates the leaching process of the component DEP into the drinking water. Studies conducted on the bottled waters showed different brands indicated the characteristics of water are shown in Table II [21].

TABLE II
DIFFERENT CHARACTERISTICS OF DIFFERENT BRANDS OF WATER, ADOPTED FROM [21]

	Brands of bottled waters					
	A	B	C	D	E	G
Bottle characteristics						
Bottle type	PET	PET	PET	PET	PET	PC
Color[1]	CL	CL	CL	CL	LB	LB
Resin identification code	1	1	1	1	1	7
Volume (L)	1	1	1	1	1	18.9
Caps[2] (color/resin code)	DB (2)	-	LB (2)	W (13)	DB (PE)	LB
Water characteristics						
Water type[2]	NMW	NMW	NMW	NMW	BDW	NMW
EC (µS/cm)	392	448	472	671	665	408
pH	7.6	7.5	7.42	8.1	7.3	8.1
Hardness (mg/L)	183	228	250	330	313	210
CO_3^{2-} (mg/L)	ND	ND	ND	ND	ND	ND
SiO_2 (mg/L)	ND	ND	ND	ND	ND	ND
$Fe^{2+\,3+}$ (mg/L)	ND	ND	ND	<0.10	ND	ND
NH_4^+ (mg/L)	<0.26	<0.2	<0.26	<0.26	ND	ND
Cl^- (mg/L)	8.8	6.91	9.42	39.7	24	4.0
Na^+ (mg/L)	9	6.56	6.9	17.1	21	2.4
K^+ (mg/L)	1.2	<2	0.78	0.8	1.4	1.2
Ca^{2+} (mg/L)	64.6	66.33	95.07	11.3	45	78.6
Mg^{2+} (mg/L)	5.3	21.3	0.92	73.4	49	3.4
HCO_3^- (mg/L)	223	262	290	383	372	ND
SO_4^{2-} (mg/L)	16.5	9.99	2	6.8	15	9.3
NO^{3-} (mg/L)	<5	9.15	5	6.9	11	7.2
NO^{2-} (mg/L)	<0.05	<0.05	<0.05	<0.05	ND	ND

ND, not detected
[1] CL, clear; LB, light blue; DB, dark blue; W, white
[2] NMW, natural mineral water; BDW, bottled drinking water

This study was used to examine the leaching of the chemicals in water at different intervals, which were: immediately upon purchase, fifteen days afterwards and thirty days afterwards. The atmospheric conditions for the fifteen day interval were 9.780 W/m^2 radiation, 180 h sunshine and 15-38˚C temperature. For the thirty day interval, the atmospheric conditions were recorded as 20.07 W/m2 radiation, 36 h sunshine and 18-40˚C temperature. Gas chromatography and ion trap mass spectrum were used for the analysis. The results showed that DEP was found at a concentration of 33 ng/L. The integrated Risk Information System (IRIS) of USEPA stated values for reference dose for chronic oral exposure for DEP to be equal to $8x10^{-1}$ mg/kg bw/day. It was found that the daily intake of DEP's was far below the maximum safe dose, therefore, the factor of safety was calculated to be relatively high. This can be observed in Table III [21]. However, it could be different for other countries.

Similarly, a study by performed by Bach et al. was used to measure the DEP concentration in the water (2011). Under the conditions shown in the table below the concentration was 0.054-0.1 for still water, <0.04-0 for mineral water and 0.082-0.355 for water (Table IV) [22].

Furthermore, a previous study conducted a research on the trace analysis of phthalates in drinking water [23]. They have determined the ultra-traces of seven phthalate compounds which several regulatory organizations have listed under research priority list. This was achieved through stir bar sorptive extraction with liquid desorption, then followed a large volume injection and capillary gas chromatography as well as mass spectrometry. Among the seven phthalates was diethyl Phthalate.

Reagents and chemicals needed were used based on the updated US EPA 525 standards for phthalate ester mix (such as diethyl phthalate), which is 500 µg/mL in methanol for each compound tested. The following standard was used neat certified bis (1-octyl) phthalate (BOP) (96.4%; Lot: 9141X, no.36938) standard were used. The results documented for DEP are shown in Tables V & VI.

The abundance of phthalates was found from the Mass fragmentograms (Fig. 2). Although the samples of the ultra-pure water were increased to 0.40 mg/L for DEP and DMP, the responses obtained from the mass fragmentogram were extremely low.

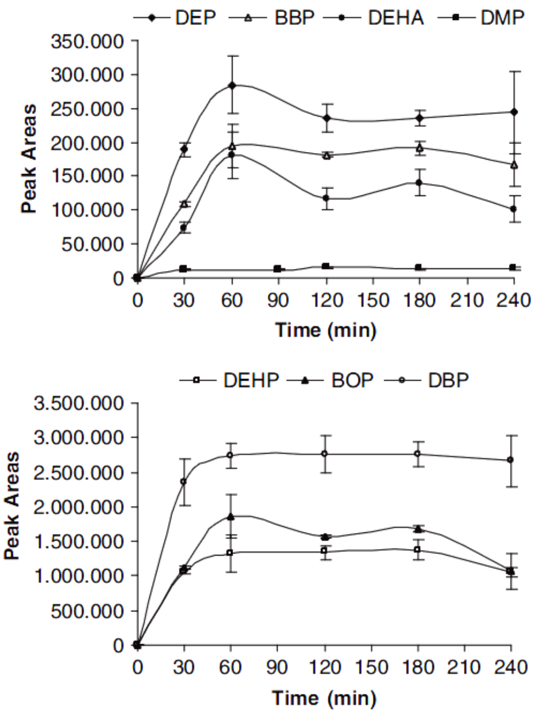

Fig. 2 Equilibrium-time profiles for the seven phthalates by SBSE-LD/LVI-GC-MS(SIM) at the 0.40 µg/L level (1000 rpm; LD solvent: MeOH) [23]

Background contamination levels were measured by taking blanks. Since ultra-pure water was used, the amounts of phthalate are negligible. From the fragmentogram, it can be observed that the quantity of DEP and DEHP are the main contaminants in the water. Based on the increasing levels of occurrence, the main source of phthalate contamination was the ethyl acetates. The LOD methodology was used to set the minimum amount of each phthalate component to be identified. It can be observed that the maximum recovery for DEP was 50% [23].

There were other routes of exposure may add to the availability of the DEP in the water. It is essential that the exposure assessment be done based on the all the routes of exposure. However, as observed in these studies, bottle water contains a significant amount of DEP in the water. In the GCC countries, people are predominantly exposed to PET bottled water since it is the main and at times the only sources of drinking water. So, the exposure level is significantly high.

TABLE III
ESTIMATION OF EXPOSURE OF EDCS IN DRINKING WATER CONSUMPTION [21]

	DEHP	DEP	BPA	NP
Max concentration (µg/L)	0.580	0.070	0.170	0.150
Daily intake via drinking water (µg/kg bw/day)	0.019	0.002	0.006	0.005
Drinking water guidelines (µg/L)	8/6		100	0.5
Calculated safety factor	13.7/10.3		588	3.3
Tolerable daily intake (TDI, µg/kg bw)	50		50	5
Contribution via drinking water (%)	0.038		0.012	0.1
Reference dose (RfD, mg/kg bw/day)	$2x10^{-2}$	$8x10^{-1}$	$5x10^{-2}$	
Calculated safety factor	$10.5x10^{2}$	$4.0x10^{5}$	$8.3x10^{3}$	
Drinking water unit risk (per µg/L)	$4.0x10^{-7}$			
Calculated carcinogenic risk	$2.3x10^{-7}$			

TABLE IV
RESULTS OF PHTHALATE ESTERS MIGRATION FROM PET INTO BOTTLED WATER [22]

Compound name	Simulant	Exposure temperature	Exposure conditions	Concentration range (µg/L)	Concentration mean (µg/L)	Reference
DEP	Still water	Refrigerated	-	0.054-0.1	0.077±0.016	
	Mineral water	22 °C	30 days	<0.04-1	0.11	
	water	Up to 30 °C	10 weeks	0.082-0.355	0.214	

TABLE V
RESULTS OF DEP [23]

Phthalates	SIM ions	RT	Linear range	r^2	LOD (µg/L)
Diethyl phthalate (DEP)	149/177	10.44	1.2-150.0	0.9970	0.30

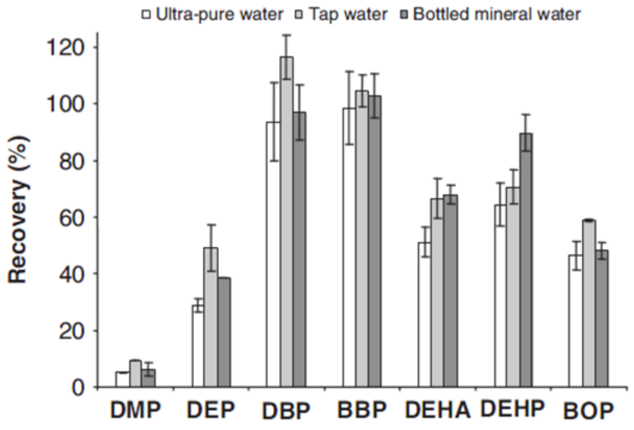

Fig. 3 Recovery yields in ultra-pure, tap and bottled water [23]

Therefore the acceptable concentrations would be significantly lower than other countries in Europe and North America.

IV. Risk Characterization

From the discussions of toxicity and exposure of DEP, it is evident that there is a strong possibility of the presence of DEP consumptions in GCC countries would be higher than the oral exposure reference dose of $8x10^{-1}$ mg/kg bw/day. With a high level of bottled water consumption in GCC, it is important to investigate whether the actual chronic daily intake is more than the no observed effects concentration or not.

V. Risk Management

In order to ensure human safety, there remain various points to be explored. Sufficient clear and relevant research should be done regarding toxicology. Also, experiments have been done on mammals, and the exposure effect observed. However, the practicality of deducing the same results on human beings should be explored. This is due to the similarities and differences between the digestive system and internal structure of mammals and humans. Differences in the digestion process may significantly affect the results. Furthermore, the theoretical reactions, allergies or effects may be comparable, but real life observations may differ. It is the human health effect that is the main concern as their exposure is higher. In addition, the pharmacokinetic aspect should also be evaluated. In other words, the effect of the human body on the chemical should be studied, and both the short and long term effects to be observed. Based on that, recommendations maybe made. The difference and effect of following the recommendations may be studied and the benefits, if any, determined.

In GCC countries, temperatures are often very high compared to other parts of world. As part of the management strategy, it is essential to observe whether the temperature can play an important role in managing the leaching of DEP from the drinking water bottles.

VI. Conclusion

The study showed that DEP leaches from PET bottled water. However, it is at a rate lower than what can be described dangerous to the countries in the West. However, in GCC countries it can still pose some threat to the humans. A case study regarding the component diethyl phthalate that was conducted in the gulf region (KSA) was presented in order to showcase the importance and procedures involved in this era. Toxicity and exposure assessments showed there is viable routes DEP toxicity to human. Therefore, it is essential to manage the risk of DEP on human health in the GCC.

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References

[1] K.Stambaugh, “What type of Water Bottle should we be using?”, Bottled Water, Page 3 – 6, (http://www.back2tap.com/wp-content/uploads/2010/11/Bottled-Water-Facts-Updated-2010.pdf)
[2] S.H. Masood, and V. KeshavaMurthy, “Development of collapsible PET water fountain bottles”, Journal of Materials Processing Technology, Vol. 162–163, 2005, pp. 83-89.
[3] B. Berry. “Can I Reuse a Plastic Water Bottle Over & Over?” (http://greenliving.nationalgeographic.com/can-reuse-plastic-water-bottle-over-over-2311.html)
[4] J. E. Cooper, E. L. Kendig, & S. M. Belcher, “Assessment of bisphenol A released from reusable plastic, aluminium and stainless steel water bottles”, Chemosphere, Vol. 85, Issue 6, October 2011, pp. 943-947.
[5] S. Keresztes, E. Tatár, V. G. Mihucz, I. Virág, C. Majdik, & G. Záray, “Leaching of antimony from polyethylene terephthalate (PET) bottles into mineral water”, Science of The Total Environment, Vol. 407, Issue 16, 1 August 2009, pp. 4731-4735.
[6] Y. Guo, “GCC PET bottle chip demand seen stable to soft in Q3 (http://www.icis.com/Articles/2010/08/13/9384768/gcc-pet-bottle-chip-demand-seen-stable-to-soft-in-q3.html)
[7] H. F. Smyth, H. F. Smyth Jr., Investigation of certain plasticizers: Report 1. Acute toxicity to small animals, Wilmington, DE: E.I. DuPont DeNemours and Co., Inc. EPA/OTS document no. 87211708, 1931.
[8] J. Bošnir, D. Puntari, A. Gali, I. Škes, T. Dijani, M. Klari, M. Grgi, M. Urkovi, & Z. Šmit, “Migration of phthalates from plastic containers into soft drinks and mineral water”, Food Technology and Biotechnology, vol. 45, 2007, pp. 91-95.
[9] P. Schmid, M. Kohler, R. Meierhofer, S. Luzi, & M. Wegelin, “Does the reuse of PET bottles during solar water disinfection pose a health risk due to the migration of plasticisers and other chemicals into the water?”, Water Research, vol. 42, 2008, pp. 5054-5060.
[10] D. Amiridou, & D. Voutsa, “Alkylphenols and phthalates in bottled waters”, Journal of Hazardous Materials, vol. 185, 2011, pp. 281-286.
[11] USEPA, “Diethyl Pthalate (CASRN 84-66-2)” (http://www.epa.gov/iris/subst/0226.htm)
[12] Hitachi Plant Technologies, Ltd. “Production process for polyethylene terephthalate (PET)” (http://www.hitachi-pt.com/products/ip/process/pet.html)
[13] Wikipedia “Polyethylene terephthalate” (http://en.wikipedia.org/wiki/Polyethylene_terephthalate)
[14] L. Sax “Polyethylene Terephthalate May Yield Endocrine Disruptor”, Environmental Health Perspectives, Vol. 118, No. 4, pp. 445-453.
[15] D. Brown, K. R. Butterworth, & I. F. Gaunt, “Short-term oral toxicity study of diethyl phthalate in the rat,” Food and Cosmetic Toxicology, vol. 16, pp. 415-422, 1978.
[16] S. Oishi, & K. Hiraga, “Testicular atrophy induced by phthalic acid esters: Effect on testosterone and zinc concentrations,” Toxicology and Applied Pharmacology, vol. 53, pp. 35-41, 1980.
[17] T. J. Gray & K. R. Butterworth, “Testicular atrophy produced by phthalate esters,” Archives of Toxicological Supplement, vol. 4, pp. 452-455, 1980.

[18] J. C. Lamb, C. Chapin, & R. E. Teague, “Reproductive effects of four phthalic acid esters in the mouse,” Toxicology and Applied Pharmacology, vol. 88, pp. 225-269, 1987.
[19] C. Pereira, K. Mapuskar, & C. Rao, “Chronic toxicity of diethyl phthalate in male Wistar rats—A dose–response study,” Regulatory Toxicology and Pharmacology, vol. 45, pp. 169–177, 2006.
[20] ATSDR “Public Health Statement Diethyl Phthalate”, (http://www.atsdr.cdc.gov/ToxProfiles/tp73-c1-b.pdf)
[21] D. Amiridou, & D. Voutsa, “Alkylphenols and phthalates in bottled waters,” Journal of Hazardous Materials, vol. 185, pp. 281-286, 2011.
[22] C. Bacha, X. Dauchya, M.Chagnonc, & S. Etienneb, “Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed,” Water Research, vol. 46, pp. 571-583, 2012.
[23] P. Serôdio, J. M. Nogueira, “Considerations on ultra-trace analysis of phthalates in drinking water,” Water Research, vol. 40, pp. 2572-2582, 2006.