Food Measure (2017) 11:818–826
DOI 10.1007/s11694-016-9453-6

ORIGINAL PAPER

Monitoring phthalates leaching into polyethylene terephthalate sterilized bottled water by ionizing radiation

M. Abboudi[1] · K. Aljoumaa[2] · A. Odeh[3] · A. Alkaid[1] · Y. Koudsi[4,5]

Received: 20 April 2016 / Accepted: 26 November 2016 / Published online: 3 February 2017

Abstract Water from a single natural spring filled in PET has been used to examine the sterilization effect of Gamma and E-Beam irradiation on the chemical and microbial quality of water through 6 months of storage under real consumer conditions. Two strategies were adapted in this work; the first was the sterilization of PET empty bottles at 20 kGy dose which were then filled by UV sterilized water. The second was the sterilization of the PET bottled water at the recommended microbial decontamination dose of 5 kGy. Dibutyl phthalate, diethyl phthalate, and dimethyl phthalate concentrations increased significantly during storage under sunlight exposure in comparison with a dark laboratory storage. Nitrite was only presented in PET bottled water that was sterilized by Gamma irradiation and stored in the dark. 5 kGy dose could be considered good for microbial sterilization of PET bottled water and has less impact on leaching of phthalates compounds than 20 kGy dose. Moreover, it could be an emergent method for water decontamination at an industrial level and consequently improve the public health.

✉ M. Abboudi
ascientific1@aec.org.sy

[1] Environmental Applications Division, Department of Radiation Technology, Atomic Energy Commission of Syria, Damascus, Syria

[2] Polymer Technologies Division, Department of Radiation Technology, Atomic Energy Commission of Syria, Damascus, Syria

[3] Analytical Chemistry Division, Department of Chemistry, Atomic Energy Commission of Syria, Damascus, Syria

[4] Atomic Energy Commission of Syria, Damascus, Syria

[5] Faculty of science, University of Damascus, Damascus, Syria

Keywords PET-bottled water · Gamma irradiation · Electron-beam irradiation · Phthalates leaching

Introduction

Over one billion people lack access to safe drinking water, and digestive tract diseases such as diarrhoea cause child deaths [1]. In recent years, there has been an immense increase in consumer demand for bottled water as an alternative to the tap water, particularly in countries having water shortage [2, 3]. Bottled water reduces or eliminates infectious organisms and prevents infection or other gastrointestinal illness [4]. Bottled water quality is influenced by many factors, [5] and the microbiological quality of bottled water is considered one of the most important criteria for water safety. Natural spring water could be a possible source of microbial and chemical contamination that may occur during bolting process of or by poor conditions of storage [5, 6]. Sources of water pollution provoked researches to find ways to grant the safety of bottled water. Previous studies reported a significant reduction in bacteria load found in bottled water by physical (UV, Ozone, sunlight exposure) or chemical treatment (chlorine). The PET bottles are exposed to sunlight for disinfection and deactivation of bacteria and to protect the consumers from diarrheal diseases [4, 7–12]. The exposure of plastic bottles to sunlight for several hours makes a pasteurizing effect of heat rather than a UV penetration [8]. However, sunlight exposure has other effects on the leaching of several carbonyl compounds, acetone, oligomers, antimony, bisphenol A, and residual monomers (phthalates) into bottled water [6, 8, 13–15], which could affect public health. Phthalates are a class of chemicals that have many implications due to their estrogenic and very poorly biodegradable properties.

They can also bio-accumulate in various human tissues and in the food chain and its contamination comes from various possible sources.

Phthalates (PAEs) have potential impacts on public health due to their presence in the environment, atmospheric aerosols, and air in several industrial applications products [16]. Exposure to phthalates via oral intake for prolonged periods could be seriously hurting the health [17]. Since phthalates were incorporated in the PET polymer matrix, these can easily migrate into drinking water during storage [3, 18]. The phthalates in beverages could be determined using different chromatography techniques as gas chromatography-mass spectrometry (GC-MS) [19].

Some organizations have regulated the guideline values of phthalates in drinking water in China: 3, and 300 µg/L for DBP, and DEP, respectively; in Japan 200 µg/L for DBP [20]. The Toxic Substances and the Disease Registry Agency determined the Minimal Risk Levels (MRLs) for DEP and DBP by oral mean; the MRLs were determined at 7 and 0.5 mg/Kg b.w(body.weight)/day, respectively [21].

The ionization irradiation appeared as an emergent technology in industry that was recommended by FAO/IAEA/WHO [22–24] for microbial decontamination in food and in many pharmaceutical products [25–27] and for wastewater disinfection [28]. Moreover, Gamma irradiation and electron-beam techniques could be used for sterilization of polyethylene terephthalate bottles. The recognized and recommended dose of gamma irradiation for the improvement of the hygienic requirement for the microbial quality control and sterilization is 10 and 25 KGy, respectively [28–30].

Storage and sunlight exposure have an impact on the migration of phthalates compounds [31–33]. Thus, in the current study, the direct and indirect effects of sterilization (during 6 months of storage) of PET bottled water (using ionized irradiation) on the leaching of some PHTs into the water and microbial quality at economic industrial ways were investigated.

Materials and methods

Sampling preparation

Drinking water bottles of a volume of 1.5 L which fabricated from Semi-crystalline PET (SABIC®PET BC-112 grade, intrinsic viscosity: 0.84 ± 0.02 Dl/g, melting range: 246–256 °C, crystalline density <1390 kg/m^3, Bulk density: 838 ± 10 kg/m^3) were used in this study.

Two protocols of sterilization were used. The first aimed to separately sterilize the empty PET bottles (B1, B2, B3) (Table 1) and the water. The sterilization of PET bottles was done by the recommended irradiation dose [28] of 20 kGy using Gamma ^{60}CO facility (Russian Type: 87 ROBO) with a dose rate of 3.88 kGy/h and Electron beam accelerator at a dose of 20 kGy) Rhodotron TT200; beam energy ≈ 2.6 MeV; dose rate = 10 kGy/min), 10 mA, 10 M. min^{-1}. While water was sterilized by a UV source at the local company of bottled water.

Table 1 Represent the sterilization treatment of empty PET bottles and PET bottled water used in the two different protocols of sterilization

Bottles Group	Sterilization treatment
B1	Control of the first protocol
B2	Empty PET bottle irradiated by gamma at dose of 20 kGy
B3	Empty PET bottle Irradiated by E-beam at dose of 20 kGy
BW1	Control of the second protocol
BW2	PET bottled water irradiated by gamma at dose of 5 kGy

The second protocol aimed to sterilize the filled PET bottles (BW1, BW2) (Table 1) with the bacterial decontamination recommended dose of 5 kGy. Gamma irradiation was only used to sterilize the Filled Bottles. Electron beam accelerator was not suitable for a microbial decontamination in one-filled bottles, as it cannot provide enough sterilization through the PET from side to another. As known, UV irradiation cannot penetrate into PET bottle, which contains anti UV agents, and therefore the UV irradiation could not be considered as an efficient method to sterilize PET bottled water.

Half of the PET bottles was placed in the laboratory and kept at ambient temperature (22 ± 2 °C) in darkness; the second half was placed individually and vertically outdoors in an open place under direct sunlight exposure with a distance of 40 cm between each of them to prevent shading. The natural spring PET bottled water was stored for 1, 37, 80, 114, 160, 184 days.

Triplicate bottles for each date and triplicate aliquots of each water sample were analyzed. A conductivity meter (Mettler TOLEDO, S30 from Switzerland) was used at 25 °C to determine the main chemical characteristics of natural spring water stored in PET bottles (pH, Total Dissolved Solid (TDS)).

Solar irradiation measurements

The irradiance was measured daily by noon across the Ultraviolet-B (UV-B, 280-315nm), and Ultraviolet-A (UV-A, 315-400nm) spectral regions using a portable HD2102.2 radiometer (Delta OHM, Italy). Measurements were made at the same place where bottles were stored and sensors were placed vertically on the ground. Daily air temperature

was measured at noon using a Hygrometer Testo 608-H1 (Testo, AG, Germany) [6].

Microbiological analysis

The microbiological test of the natural spring bottled water was carried out during 1, 37, 80, 114, 160 and 184 days of storage under incubation conditions. The total bacterial counts as colony forming units (CFU) was determined using pour plate method; the plates were incubated at 37 °C for 48 h. The total Coliforms counts were determined by eosin methylene blue (Himedia Labs, India) agar plates, the plates were incubated at 22 and 37 °C for 24 h. Lurial Broth (Himedia Labs, India) determined the *E. coli* count at 37 °C for 24 h [6, 34].

Determination of anions and cations

Water samples were injected into an ion chromatograph (850 professional IC, Metrohm, Herisau, Switzerland) with an injection volume of 10 µL. The column for cation analysis was Metro Sep C2-150 (150 × 4.0 mm, 5 µm). The mobile phase was 4 mmol/L tartaric acid and 0.75 mmol/L (2,6-pyridinedicarboxylic acid 99%). For anion analysis, the column was Metro Sep A–supp 5 (100 × 4.0 mm, 5 µm) and the mobile phase was 3.2 mmol/L sodium carbonate and 1 mmol/L sodium hydrogen carbonate. The detection limit of all cations and anions was about 0.5 mg/L [6].

Analyses of phthalates

An Agilent 6890 gas chromatograph coupled with a 5973 N inert mass-selective detector with auto-sampler was used for dimethyl phthalate (DMP), di-butyl phthalate (DBP), and diethyl phthalate (DEP) analysis. Separation was achieved on a DB-5MS capillary column (3.0 m × 0.25 mm, 0.25 m, Agilent Technologies, USA). Ultra-pure helium (99.999%) was used as a carrier gas at a flow rate of 0.9 mL min. The target solution (1 µL) was injected into the GC system coupled to a mass spectrometry detector operated in a positive electron ionization mode with ionization energy of 70 eV. The initial temperature was 250 °C and the injection was accomplished in splitless mode (splitless time: 1 min). The separation was run at a 0.9 mL min^{-1} flow rate. The oven temperature program was: from 95 °C (2 min) to 150 °C (2 min) at 2 °C/min, then to 250 °C (5 min) at 4 °C/min. The transfer line and ion source temperatures were set at 280 and 250 °C, respectively. Chromatograms were recorded in a Scan mode [35, 36] and performance of the employed analytical method was checked by evaluating the following parameters: limits of detection (LOD), limits of quantification (LOQ), recovery and repeatability. Repeatability were estimated for all Phthalates compounds (n = 6) and expressed as a relative standard deviation (RSD%). For recovery studies, two concentration levels of Phthalates compounds were tested: lower level (1 mg kg^{-1}) and upper level (10 mg kg^{-1}). The results of repeatability and recoveries were satisfactory ranging from 70 to 85%. The repeatability was acceptable (RSD between 3.2 and 11.0%) for this kind of complex sample.

Statistical analysis

Data were subjected to the statistical analysis of Student's *t* test, $p < 0.05$ using the SUPERANOVA computer package (Abacus Concepts Inc, Berkeley, CA, USA; 1998).

Results and discussion

Solar irradiation measurements

The instantaneous intensity of UV-B and UV-A of sunlight were recorded at the place of bottle storage due to their importance which is the most active parameters in plastic photo-degradation [6]. Ambient UV-B intensity was at the maximum 2.8 W/m^2 at the beginning of the measurement phase in July 2014, UV-B intensity gradually decreased to reach 0.12 W/m^2 after 184 days of storage (6 months). Similar trend was observed for UV-A with a maximum intensity of 28.5 W/m^2 in July 2014, and decreased to 2.5 W/m^2 toward the end of the storage period. These results are consistent with our previous work [34] and confirm the climate change cycle [6].

Microbial and chemical properties of treated water following the by first protocol of sterilization

Results of the microbiological quality of water confirm that the water was sterile with a load of: 0 CFU/100 mL of *E. coli*, 0 CFU/100 mL of total Coliforms and less than 10 CFU/100 mL of total count [6] and remains sterilized 184 days post storage.

The chemical analysis for the PET bottled water show the following results; TDS values ranged between 197.7 ± 0.3 and 202.0 ± 0.5 mg/L and pH values changed from 8.1 to 7.7. There was no significant changes in TDS values between treated and non-treated PET bottled water, and then observed difference between water bottles stored in the dark and those exposed to sunlight directly (*t* test, $p < 0.05$) was not significant (Table 2). The change in anions and cations compositions were determined during the 184 days of storage.

The values of fluoride, chloride, nitrate, sulphate, sodium, potassium, calcium and magnesium ions were:

Table 2 Change in anions, cations and TDS concentration (mg/L) in the empty PET bottles filled with sterilized water during 184 days of storage in the laboratory (Dark) and under sunlight exposure (Sun)

	Days	1	37		80		114		160		184	
	Sample	Dark	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun
F^- (mg/L) ± 0.01[a]	B1	0.10	0.10	0.10	0.09	0.09	0.12	0.13	0.10	0.10	0.10	0.11
	B2	0.10	0.10	0.11	0.09	0.11	0.12	0.13	0.10	0.10	0.10	0.11
	B3	0.10	0.10	0.11	0.09	0.11	0.12	0.13	0.11	0.10	0.09	0.10
Cl^- (mg/L) ± 0.5[a]	B1	10.6	10.7	11.1	10.6	10.5	11.8	12.3	11.6	11.7	11.8	11.6
	B2	10.6	10.7	11.0	10.6	11.8	11.8	12.1	11.4	11.7	11.9	11.1
	B3	10.6	10.7	10.9	10.6	11.8	12.0	12.1	11.4	11.7	11.6	11.4
NO_3^- (mg/L) ± 0.7[a]	B1	16.5	16.7	16.6	16.2	16.0	19.2	19.8	17.4	17.5	21.8	18.0
	B2	16.8	17.0	17.2	16.5	18.8	19.3	19.8	17.3	17.8	21.2	21.9
	B3	16.7	17.0	17.2	16.4	18.5	19.6	19.8	17.9	17.7	22.2	22.7
SO_4^{2-} (mg/L) ± 0.4[a]	B1	6.8	7.0	7.0	6.5	6.5	8.0	8.7	7.0	7.0	7.9	7.2
	B2	6.8	7.1	6.8	6.5	7.6	7.8	8.8	6.6	7.1	8.0	7.8
	B3	6.8	7.1	7.1	6.5	7.5	7.9	8.8	8.0	7.0	7.8	8.0
Na^+ (mg/L) ± 0.3[a]	B1	4.3	4.8	4.6	5.0	4.4	3.7	4.4	4.7	4.2	4.4	4.5
	B2	5.1	4.7	4.3	4.7	4.6	4.3	4.4	4.3	4.5	4.5	4.3
	B3	4.3	4.2	5.5	4.9	4.2	4.8	4.5	4.4	4.2	4.6	4.5
K^+ (mg/L) ± 0.03[a]	B1	0.34	0.33	0.34	0.35	0.35	0.33	0.33	0.33	0.32	0.34	0.32
	B2	0.35	0.34	0.34	0.35	0.36	0.32	0.32	0.33	0.36	0.34	0.36
	B3	0.35	0.35	0.38	0.33	0.34	0.33	0.37	0.32	0.31	0.33	0.31
Ca^{2+} (mg/L) ± 0.6[a]	B1	23.9	19.8	19.7	20.3	21.4	19.8	25.6	18.1	19.1	17.4	17.8
	B2	19.4	19.6	19.7	19.4	19.8	19.7	19.5	17.5	19.0	18.0	17.8
	B3	21.0	20.1	20.0	19.5	22.3	26.9	19.3	17.1	18.7	16.9	17.5
Mg^{2+} (mg/L) ± 0.8[a]	B1	19.1	18.6	18.7	18.6	18.0	18.1	18.5	18.9	18.5	18.3	18.5
	B2	18.8	18.8	18.6	18.3	17.8	18.6	18.6	18.5	18.2	19.0	19.0
	B3	18.6	18.4	18.1	18.4	18.2	18.1	18.6	18.3	18.4	19.0	18.2
TDS (mg/L) ± 0.5[a]	B1	200.7	199.6	201.0	198.0	198.3	198.8	199.6	198.9	200.0	199.8	196.5
	B2	200.2	200.2	200.2	197.7	198.5	197.8	199.9	197.6	198.5	198.1	197.6
	B3	202.0	201.7	201.7	197.3	197.8	198.8	199.4	198.2	199.4	196.0	196.8

[a]Maximum value of estimated errors during measurements for each anions/cations

0.10–0.13, 10.6–12.0, 16.5–22.7, 6.8–8.8, 4.3–4.5, 0.34–0.36, 17.5–23.9 and 18.8–19.1 mg/L, respectively.

Chloride, nitrate, and sulphate ions increased with the storage time where calcium ions decreased after 184 days of storage. Differences in anions and cations composition under the aforementioned conditions of storage had negligible significant values (*t* test, $p < 0.05$).

Similar changes in concentrations for some anions and cations in PET bottled water were also observed after sunlight exposure for 30 days [37]. The total measured anions and cations in this work form only ~20% from the other anions and cations, which were included in the TDS values calculation, therefore, the differences in anions and cations composition had no effect on TDS values.

Figure 1 shows the leaching of phthalates detected during storage in all bottles sterilized by the first method. Results demonstrate that no traces of phthalate were noticed in the first 40 days of storage. Similar results were also reported by [38]. Moreover, DBP, DEP and DMP increased clearly after 114 days of storage as presented by Bach [33] and continued until the end of storage time (184 days), but no significant difference in the DBP concentration between the empty PET sterilized by gamma radiation (B2) and those sterilized by E-beam (B3) in comparison with blanks (B1) (*t* test, $p < 0.05$). In addition, there was no significant difference in the DEP concentration in all PET bottles stored under sunlight (*t* test, $p < 0.05$), B3 samples showed higher DEP concentration than B2 and B1 samples stored in the dark. The DMP concentration versus time has the same tendency as DEP .The final concentration of DBP, DEP and DMP at 184 days was higher under the sunlight exposure compared with dark storage. The concentration of DBP, DEP and DMP increased respectively by was around 280, 190 and 140% higher in the samples stored in sunlight compared those stored in dark, respectively. The sunlight could accelerate the leaching of phthalates compounds; this

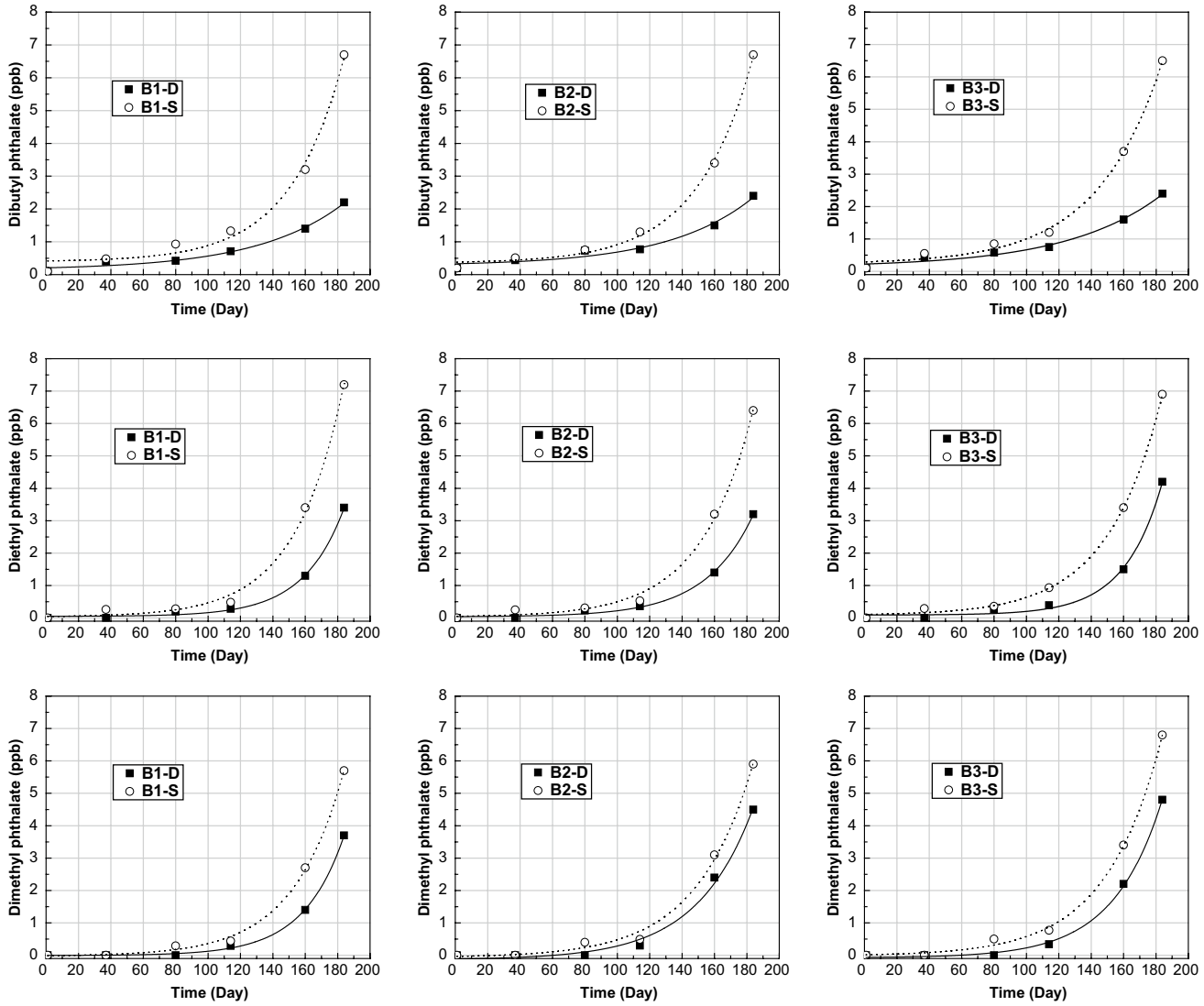

Fig. 1 Variation of the concentration of DPP, DEP and DMP in PET bottled water during the storage for 184 days, *B1* control, *B2* sterilized PET bottles at 20 kGy by Gamma irradiation, *B3* sterilized PET bottles at 20 kGy by E-beam. [*d* storage in laboratory (*Dark*); *s* storage under sunlight exposure (*Sun*)]

effect was noted on carbonyl compounds in the PET bottled water [6].

Leaching kinetic model

Several kinetics models were studied to match the aforementioned results of phthalates leaching during the time of this study [14, 39, 40]. It was found to be controlled by exponential growing function, which gave a good fitting ($R^2 > 0.97$), Fig. 1. The concentration of each phthalates compounds in water versus the water contact time (t) can be approximately described by the equation:

$$C = A\, e^{t/\tau} + C_0$$

where C, C_0 the concentration of phthalates, A constant, τ: time constant (doubling time).

The results of the fitting using last equation were summarized in the (Table 3).

A contrary effect on the doubling time constant due to sunlight exposure can be noticed, where DBP is decreased from ~55 to 36 while are slightly increased DEP and DMP. This indicated that sunlight exposure affects DBP leaching more than other phthalic compounds.

Table 3 Fitting constant of different phthalates compounds

			C_0	τ	R^2
DBP	B1	Dark	0.14	53.6	0.98
		Sun	0.39	33.2	0.99
	B2	Dark	0.27	52.3	0.97
		Sun	0.35	34.8	0.99
	B3	Dark	0.13	58.6	0.98
		Sun	0.23	40.3	0.99
DEP	B1	Dark	0.05	25.0	0.99
		Sun	0.03	30.0	0.99
	B2	Dark	0.04	29.6	0.99
		Sun	0.03	32.2	0.99
	B3	Dark	0.09	23.3	0.99
		Sun	0.08	33.5	0.99
DMP	B1	Dark	−0.01	25.2	0.99
		Sun	−0.03	31.3	0.99
	B2	Dark	−0.14	34.9	0.99
		Sun	−0.07	35.1	0.99
	B3	Dark	−0.08	30.3	0.99
		Sun	−0.02	34.5	0.99

Table 4 Change in anions, cations and TDS concentration (mg/L) in the PET bottled water during 184 days of storage in the laboratory (Dark) and under sunlight exposure (Sun)

Ions	Days	1	37		80		114		160		184	
	Sample	Dark	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun	Dark	Sun
F^- (mg/L) ±0.01[a]	BW1	0.10	0.10	0.11	0.09	0.09	0.12	0.13	0.10	0.10	0.11	0.11
	BW2	0.10	0.10	0.11	0.09	0.09	0.12	0.12	0.10	0.10	0.10	0.12
Cl^- (mg/L) ±0.5[a]	BW1	10.5	10.7	11.1	10.6	10.5	11.7	12.3	11.6	11.6	11.4	11.9
	BW2	10.6	10.7	10.8	10.8	10.5	11.8	12.2	11.6	11.6	11.3	11.8
NO_3^- (mg/L) ±0.7[a]	BW1	16.4	16.7	16.9	16.2	16.1	19.2	19.9	17.3	17.5	22.2	18.2
	BW2	13.6	14.2	16.9	14.6	16.2	15.9	19.8	14.2	17.5	18.0	18.2
NO_2^- (mg/L) ±0.5[a]	BW1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	BW2	8.3	7.7	0.1	8.2	0.1	9.6	0.2	8.8	0.2	9.5	0.2
SO_4^{2-} (mg/L) ±0.4[a]	BW1	6.7	7.2	7.0	6.5	6.5	8.0	8.9	7.0	6.8	8.0	7.5
	BW2	6.8	7.1	7.0	6.5	6.5	8.0	6.0	7.0	6.8	8.1	7.5
Na^+ (mg/L) ±0.3[a]	BW1	4.7	4.0	4.3	4.4	4.0	4.2	4.4	4.4	4.4	4.3	4.4
	BW2	4.3	4.1	5.1	4.4	4.3	4.2	4.4	4.3	4.5	4.4	4.4
K^+ (mg/L) ±0.03[a]	BW1	0.34	0.34	0.40	0.34	0.35	0.34	0.34	0.34	0.87	0.33	0.34
	BW2	0.35	0.33	0.40	0.35	0.36	0.33	0.33	0.33	0.31	0.32	0.32
Ca^{2+} (mg/L) ±0.6[a]	BW1	24.0	19.6	20.1	21.9	19.3	20.9	17.3	17.7	19.5	17.7	17.5
	BW2	25.3	19.4	19.6	19.5	19.4	20.3	18.7	17.8	19.3	17.3	17.8
Mg^{2+} (mg/L) ±0.8[a]	BW1	18.8	18.6	18.6	18.3	18.3	17.6	18.6	18.7	18.5	18.7	18.6
	BW2	18.7	18.4	18.7	18.7	18.3	17.5	18.8	18.7	18.5	18.2	18.4
TDS (mg/L) ±0.9[a]	BW1	201.3	199.5	201.0	196.7	197.8	198.9	199.7	197.4	199.9	198.2	198.0
	BW2	200.3	202.3	200.0	196.5	197.9	198.9	199.4	196.2	199.9	198.6	200.7

[a]Maximum value of estimated errors during measurements for each anions/cations

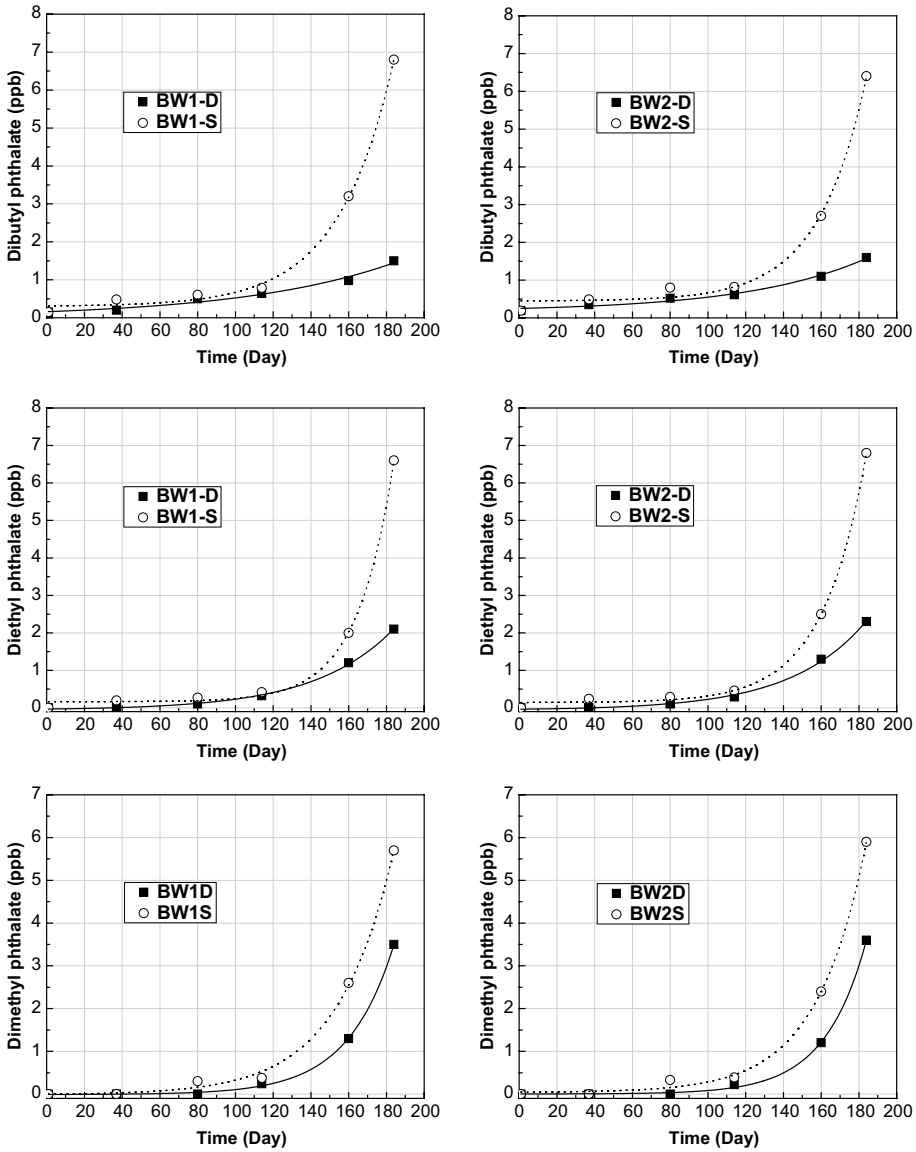

Fig. 2 Variation of the concentration of DPP, DEP, and DMP in PET bottled water during the storage for 184 days, *BW1* non-irradiated bottles, *BW2* sterilized PET bottled water at 5 kGy by gamma irradiation. [*d* storage in the laboratory (*Dark*); *s* storage under sunlight exposure (*Sun*)]

Microbial and chemical properties of treated water following the second protocol of sterilization

The PET bottled water was sterilized by gamma radiation (BW2 samples) before storage. The dose (5 kGy) was chosen to be lethal for all pathogenic bacteria [41].

The natural spring water was found to be sterile by a microbiological analysis. PET bottled water (BW2) was found to stay sterile after irradiation treatment and storage for 1, 37, 80, 114, 160 and 184 days as those non-gamma irradiated (BW1).

The chemical analysis for the PET bottled water show that there was no significant differences between TDS values (Table 4) for BW1 and BW2 PET water bottles water. In addition, there was no effect of sunlight exposure for bottles during storage (*t* test, $p < 0.05$).

The TDS values were in good agreement with those reported in the literature [6, 42]. The change in anions and cations compositions was similar to results presented in the first section of this work with negligible significant changes (t-test, $p < 0.05$). The values of Fluoride, Chloride, nitrate, sulphate, sodium, potassium, calcium and magnesium ions were ranged between 0.10–0.12, 10.5–11.9, 13.6–22.2, 6.7–8.9, 4.7–4.3, 0.32–0.35, 25.3–17.3 and 18.8–18.4 mg/L, respectively (Table 4).

The presence of nitrite was only recorded in BW2 samples (Table 4). About $60.0 \pm 0.5\%$ of nitrate transformed to nitrite when the PET bottled water was directly

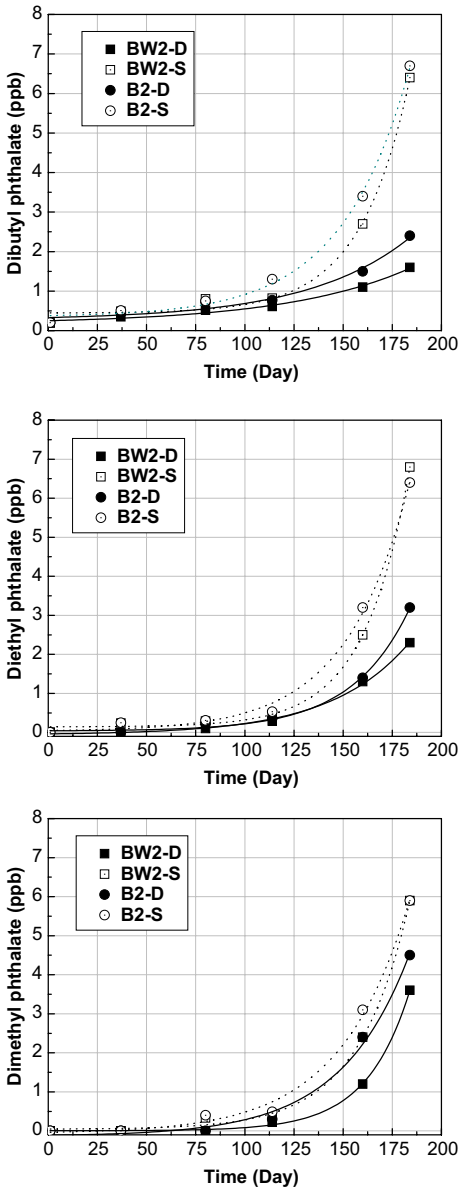

Fig. 3 Comparison between the concentration variation of DPP, DEP, and DMP in PET bottled water during the storage for 184 days, *B2* sterilized empty PET bottles at 20 kGy by Gamma, *BW2* sterilized PET bottled water at 5 kGy by Gamma irradiation [*d* storage in the laboratory (*Dark*); *s* storage under sunlight exposure (*Sun*)]

irradiated by gamma irradiation and stored in the dark, but this amount of nitrite was retransformed to nitrate (up to 98.9 ± 0.2%) under the exposure of WB2 samples to natural sunlight exposure (Table 4). Photo-nitration and photon-itrosation in aqueous solution were observed before [42, 43].

The influence of sterilizing PET bottled water by gamma irradiation on leaching of phthalates was presented in (Fig. 2). The leaching of DBP, DEP and DMP was also increased as shown in (Fig. 1) during storage. No significant difference was reported in the DBP, DEP and DMP concentration in PET bottled water (BW1) and in sterilized PET water bottles by gamma radiation (WB2) (*t* test, $p < 0.05$).The sunlight could accelerate the leaching of phthalates, The final concentrations of DBP, DEP, and DMP at 184 days post storage were significantly higher the sunlight exposure in comparison to those stored in the dark (t-test, $p < 0.05$).

Moreover, the kinetics of leaching of phthalates compound was in accordance by the equation proposed previously, and the noticed doubling time constant.

Comparison between the two means of sterilization

At microbial level: Both protocols gave excellent sterilization result of water, and we found that the water preserves its quality of sterilization during storage. A consequence of the previous results, both electron beam and gamma radiation could be reused after sterilizing PET bottles. However, Gamma irradiation could be applicable in bottled water industry due to the high penetration property in comparison with electron beam, the penetration is crucial in microbial contamination and in the technical applicability for PET bottled water industry.

Figure 3 shows the phthalates leaching tendency during storage for the two sterilization protocols using only gamma radiation (B2, BW2). The concentration of each DBP, DEP and DMP was less in BW2 in comparison with B2 in both sun and dark conditions. Otherwise, the 5 kGy dose of gamma radiation provokes fewer phthalates migration than the 20 kGy dose. At economical level, using lower dose for sterilization in one-step (protocol 2) instead of using two separated steps (protocol 1) shall be more practical and cost effective.

Conclusion

Two protocols were used to sterilize PET bottled water. Effects of sterilization protocol on of DMP, DEP and DBP leaching in bottled waters and on the microbial quality during 184 days of storage under real poor conditions of storage were monitored. The slight increase in leaching of studied phthalates started 40 days post storage under real poor condition, with a net effect of sunlight exposure compared to the dark storage in the laboratory. Similar trends for all phthalates compounds were observed. Moreover, the final concentrations of DMP, DEP, and DBP were lower than the allowed limit after 184 days of storage. The dose of gamma radiation at 5 kGy used has lower effects on the phthalate leaching than the 20 KGy that used was in the first protocol and sufficient for sterilizing bottled water during the industrial process a lower cost.

Acknowledgements The authors would like to express their deep appreciation to Prof. I. Othman (D. G. of AECS) for his encouragement. Thanks are also extended to Dr. Antonions Al-Daoude for his highly appreciated help in language editing.

References

1. R. Cidu, F. Frau, P. Tore, J. Food Comp. Anal. **24**, 184 (2011)
2. C. Bach, X. Dauchy, I. Severin, J.F. Munoz, S. Etienne, M.C. Chagnon, Food Chem. **139**, 672 (2013)
3. M.Z. Jeddi, N. Rastkari, R.A. khanih, M. Yunesian, Food Res. Int. **69**, 256 (2015)
4. G.L. Napier, C.M. Kodner, Primary Care Clin. Office Pract. **35**, 789 (2008)
5. H. Nsanze, Z. Babarinde, H.AI Kohaly, Environ. Int. **25**, 53 (1999)
6. M. Abboudi, A. Odeh, K. Aljoumaa, Toxicol. Environ. Chem. **98**, 167 (2016)
7. M.B. Fisher, M. Iriarte, K.L. Nelson, Water Resour. **4**, 1745 (2012)
8. R.M. Conroy, E.M. Meegan, T.M. Joyce, K.G. McGuigan, J. Barnes, Lancet **348**, 1695 (1999)
9. D.R.J. Colley, A. Donnison, M.D.J. Speed, C.M. Ross, J.W. Nagels, Water Resour. **33**, 1220 (1999)
10. J. Lonnen, S. Kilvington, S.C. Kehoe, F. Al-Touati, K.G. McGuigan, Water Resour. **39**, 877 (2005)
11. W. Schneider, H.H. Rump, J. Int. Ozone Assoc. **5**(2), 95–101, (1983). doi:10.1080/01919518308550973
12. M. Fisher, M. Iriarte, K.L. Nelson, Water Resour. 1745–46 (2012)
13. P. Schmid, M. Kohler, R. Meierhofer, S. Luzi, M. Wegelin, Water Resour. **42**, 5054 (2008)
14. A.S. Redzepovic, M.M. Acanski, D.N. Vujic, V.L. Lazic, Chem. Ind. Chem. Eng. Q. 18, 155 (2012)
15. A. Tukur, L. Sharp, B. Stern, C. Tizaoui, H. Benkreirc, J. Environ. Monit. 14, 1237 (2012)
16. S. Net, A. Delmont, R. Sempéré, A. Paluselli, B. Ouddane, Sci. Total Environ. **515**, 162 (2015)
17. I. Al-Saleh, R. Elkhat, J. Food Meas. Charact. 8, 373 (2014)
18. P. Otero, S.K. Saha, S. Moane, J. Barron, G. Clancy, P. Murray, J. Chromatogr. B **997**, 229 (2015)
19. I. Ustun, S. Sungur, R. Okur, A. T. Sumbul, S. Oktar, N. Yilmaz, C. Gokce. Food Anal. Methods 8(1), 222 (2015)
20. X. Liu, J. Shi, T. Bo, H. Li, J.C. Crittenden, Environ. Sci. Poll. Res. (2015). doi:10.1007/s11356-015-4253-9
21. ATSDR Agency for Toxic Substances and Disease Registry: Minimal Risk Levels (MRLs). https//www.astdr.cdc.gov. Accessed March 2016.
22. WHO *Wholesomeness of Irradiated Food. Report of a Joint FAO/IAEA WHO Expert Committee, Technical Report Series No. 659*, (World Health Organization, Geneva, 1981)
23. A.M.M.R. Afify, H.S. El-Beltagi, A. A-Aly, A.E. El-Ansary, Asian Pac. J. Trop. Biomed. **2**(3) 1548 (2012)
24. M. Abboudi, M. AL-Bachir, Y. Koudsi, H. Jouhara, Int. J. Food Prop. **19**, 1447 (2016)
25. C.K. Waje, S.Y. Jun, Y.K. Lee, B.N. Kim, D.H. Han, C. Jo, J.H. Kwon, Food Control **20**, 200 (2009)
26. R. Bhat, K.R. Sridhar, A. A. Karim, Radiat. Phys. Chem. **79**, 976 (2010)
27. M. Al-Bachir, Food Chem. **197**, 191 (2016)
28. A. T. Fintzoua, M. G. Kontominasa, A. V. Badekaa, M. R. Stahlb, K. A. Riganakos, Radiat. Phys. Chem. 76, 1147 (2007)
29. IAEA International Atomic Energy Agency: Food irradiation clearances database. http://nuclues.iaea.org/NUCLUES/Content/Applications/FICdb/DatabaseHome.jsp
30. SASMO. Syrian Arab Standard and Metrology Organization. 3512/2010.ICS 17.240 (2010)
31. S.V. Leivadara, A.D. Nikolaou, T.D. Lekkas, Food Chem. **108**, 277 (2008)
32. A. Strube, A. Buettner, C. Groetzinger, Water Sci. Technol. WST. **9**, 299 (2009)
33. C. Bach, X. Dauchy, M.C. Chagnon, S. Etienne, Water Resour. **46**, 571 (2012)
34. M. Abboudi, A. Odeh, J. Water Supply REST **64**(2), 149 (2015)
35. F. K. Kawahara, J. W. Hodgeson, in Method, ed. By J.W. Munch (U.S. Environmental Protection Agency, Cincinnati, 1995), p. 506
36. X.L. Cao, J. Chromatogr. A **1178**, 231 (2008)
37. S.G. Muhamad, L.S. Esmail, S.H. Hasan, J. Appl. Sci. Environ. Manag. **15**, 147 (2011)
38. E. Ceretti, C. Zani, I. Zerbini, L. Guzzella, M. Scaglia, V. Berna, F. Donato, S. Monarca, D. Feretti, Water Resour. **44**, 1462 (2010)
39. A.A. Baba, F.A. Adekola, E.E. Toye, R.B. Bale, J. Miner. Mater. Charact. Eng. **8**, 787 (2009)
40. Y. Wei, R.L. Brainard, Advanced Processes for 193-nm Immersion Lithography, Chap. 3: Resist Leaching and Water Uptake. (Society of photo optical instrumentation engineers (SPIE), Bellingham, 2009)
41. R.M.A. Musaad (2004). Disinfection of Sewage Water and Sludge using Gamma Radiation (Doctoral dissertation, Faculty of Science, University of Khartoum)
42. WHO. World Health Organization, *Guidelines for Drinking-water Quality, 4 edition*. (World Health Organization, Geneva, 2011)
43. F. Machado, P. Boule, J. Photochem. Photobiol. A **86**, 73 (1995)
44. A. Dejam, P. kleinbongard, T. Rassaf, S. Hamada, P. Gharini, J. Rodriguez, M. Feelisch, M. Kelm, Free Radical. Biol. Med. **35**, 1551 (2003)