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Water and Sanitation in Developing Countries (SANDEC)
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Report 429670

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Test assignment:	**Migration of organic components from polyethylene terephthalate (PET) bottles to water**
Sample material:	15 PET bottles of various origin
Client reference:	R. Meierhofer and M. Wegelin, EAWAG
Order date:	May 2, 2003
Sample material received:	May 5, 2003
Test performed:	June 2 - 18, 2003
Number of pages:	13

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STS no. 082

1 Samples

Colourless polyethylene terephthalate (PET) bottles of different origin and age were assessed in an exposure experiment (see Table 1).

Table 1: PET bottles used in the exposure experiment (used: bottle reused for solar disinfection of water, new: bottle without reuse after use for originally bottled beverage).

Bottle no.	Country of origin	Age	Size (L)	Brand	Top	Sealing
1	Honduras	used	2	-	white	light blue
2	Honduras	used	2	-	white	light blue
3	Honduras	used	1.5	-	blue	clear
4	Honduras	new	2	Coca Cola	red	light blue
5	Honduras	new	2	Coca Cola	red	light blue
6	Nepal	used	1	-	blue	without
7	Nepal	used	1	-	blue	without
8	Nepal	used	1	-	blue	without
9	Nepal	new	1	Aqua Smile	blue	without
10	Nepal	new	1	Aqua Smile	blue	without
11	Switzerland	used	1	Migros	yellow	light blue
12	Switzerland	used	1	Migros	yellow	light blue
13	Switzerland	used	1	Migros	yellow	light blue
14	Switzerland	new	1	Migros	yellow	light blue
15	Switzerland	new	1	Migros	yellow	light blue

2 Experimental

2.1 Background

The solar water disinfection (SODIS) process is a simple method to improve the microbiological quality of drinking water. SODIS uses solar radiation to destroy pathogenic micro-organisms causing water borne diseases. Contaminated water is filled into transparent plastic bottles made from PET and exposed to full sunlight for six hours.

In a previous investigation, the migration of several chemicals including the plasticizer di(2-ethyl-hexyl)adipate (DEHA, CASRN 103-23-1) from used polyethylene terephthalate (PET) bottles to drinking water stored in these bottles has been described [1]. Due to chemical background problems, the migration of di(2-ethylhexyl)phthalate (DEHP, CASRN 117-81-7) was not determined.

In the present investigation, the levels of DEHA and DEHP in water treated under SODIS conditions are determined.

2.2 Exposure experiment

Bottles were pre-rinsed and filled with distilled water (water for chromatography, Merck, Darmstadt, Germany). Exposure to sunlight was effected on June 2 and 3, 2003 at a geographical latitude of 47° 24' 14.5" N. Some of the bottles were put half-way in a water bath kept at 60°C. All bottles were exposed in horizontal position. Control bottles were kept in the shade at room temperature (25°C). The global radiation was measured using a pyranometer (type CM 3, Kipp & Zonen, Delft, The Netherlands). Exposure conditions are given in Table 2. Total time of exposure to sunlight was 17 hours, total storage time of the water in the PET bottles was 48 hours (see Appendix, Figures 1 – 6).

Table 2: Exposure conditions of PET bottles to sunlight (n.d.: not determined).

Date	Time	Temperature controlled water bath [°C]	Water temperature [°C]	Radiation (horizontal) [W/m^2]	Radiation (maximum) [W/m^2]	Remarks
June 2	09:50 a.m.	57	n.d.	194	n.d.	start of exposure
	10:17 a.m.	53	n.d.	554	n.d.	
	00:20 p.m.	55	n.d.	833	n.d.	
	03:00 p.m.	55	n.d.	811	n.d.	
	05:10 p.m.	34	34	434	n.d.	temperature controller off
June 3	08:00 a.m.	18	18	283	694	temperature controller on
	10:02 a.m.	60.7	n.d.	556	n.d.	
	11:30 a.m.	60.3	30	752	922	
	01:55 p.m.	59.7	39	845	921	
	05:05 p.m.	60	43	642	n.d.	end of exposure

2.3 Sample preparation

The water was transferred from the PET bottles to 1 L volumetric flasks pre-rinsed with water and methanol. As a method blank, three pre-rinsed 1 L volumetric flasks were filled with distilled water, taken from the same supplier and analysed. For analysis, 100 mL aliquots were collected in 100 mL pre-rinsed volumetric flasks. The internal standards (0.5 µg $^{13}C_6$-DEHA CLM-4675-1.2 and 2.5 µg $^2H_4$-DEHP DLM-1368 from Cambridge Isotope Laboratories, Andover, USA) were added, and the water was topped with 1 mL *n*-hexane. After vigorous shaking for 1 min, the samples were cooled down to 6°C. For DEHA and DEHP determination, samples were taken directly from the *n*-hexane phase. For full-scan GC/MS analysis, an aliquot of 500 µL *n*-hexane was transferred into an autosampler vial and heated to 40°C, until the volume was reduced to 20 µL.

2.4 Gas-chromatography/mass spectrometry (GC/MS)

2.4.1 Instruments

Gas chromatograph:	HRGC MEGA 2 series (Fisons)
Capillary column:	20 m × 0.28 mm, stationary phase PS 086 (polydimethyl siloxane with 12 – 15 % diphenyl siloxane), film thickness 0.15 µm
Mass spectrometer:	double focusing mass spectrometer Finnigan MAT 95

2.4.2 Experimental conditions

Carrier gas:	hydrogen, 50 kPa
Injection:	2 µL, splitless
Temperature program:	DEHA and DEHP quantification: 60°C (1 min), 20°C/min to 220°C, 4°C/min to 260°C (5 min) full-scan GC/MS analysis: 60°C (1 min), 8°C/min to 260°C (5 min)
Ion source temperature:	180°C
Ionisation:	electron ionisation (EI), positive ion mode
Electron energy:	70 eV
Mass resolution:	DEHA and DEHP quantification: m/Δm = 8'000 (10% valley) full-scan GC/MS analysis: m/Δm = 1'000 (10% valley)
Multiple ion monitoring:	DEHA and DEHP quantification: registration of the m/z values of characteristic EI fragment ions of native and isotope labelled DEHA and DEHP: DEHA: 241.1798 ($C_{14}H_{25}O_3$) DEHA: 259.1909 ($C_{14}H_{27}O_4$) $^{13}C_6$-DEHA: 247.2000 ($C_8{}^{13}C_6H_{25}O_3$) $^{13}C_6$-DEHA: 265.2111 ($C_8{}^{13}C_6H_{27}O_4$) DEHP: 279.1591 ($C_{16}H_{23}O_4$) $^2H_4$-DEHP: 283.1842 ($C_{16}H_{19}{}^2H_4O_4$)
Full-scan mass range:	m/z 33 – 500

2.5 Quantification of DEHA and DEHP

Quantification was based on signal areas in the mass chromatograms. For calibration, DEHA and DEHP purchased from Fluka (Buchs, Switzerland) were used.

2.6 Identification of further components by full-scan GC/MS analysis

Full-scan GC/MS runs were analysed by comparison with reference spectra from the "Wiley Registry of Mass Spectral Data, 6th Ed." using the software "Masslib".

2.7 Quality assurance

- The investigation was performed according to the rules of the quality management system ISO/IEC 17025.
- Detection limits (signal-to-noise ratio 3) are 0.005 µg/L for quantitative determination of DEHA and DEHP, and approx. 1 µg/L for reconstructed ion chromatograms in qualitative full-scan analyses.
- The components reported (except DEHA and DEHP) were tentatively identified by library search, only. The identity of these components needs to be confirmed by an independent analytical method using the respective reference compounds.
- Concentrations of the components reported are not necessarily proportional to their signal intensities in the respective full scan GC/MS chromatograms. Retention times may vary slightly between individual runs.

2.8 Units and acronyms

2.8.1. Units

Pressure: 1 kPa (10^3 kg m^{-1} s^{-2})
Radiation: 1 W m^{-2} (1 kg s^{-3})
Mass: 1 µg = 10^{-3} mg = 10^{-6} g = 10^{-9} kg
Volume: 1 µL = 10^{-3} mL = 10^{-6} L

2.8.2 List of acronyms

DEHA	di(2-ethylhexyl)adipate
DEHP	di(2-ethylhexyl)phthalate
EI	electron ionisation
GC/MS	gas chromatography/mass spectrometry
PET	polyethylene terephthalate
QA	quality assurance
SODIS	solar water disinfection

3 Results

3.1 Components identified by full-scan GC/MS analysis

All full-scan GC/MS chromatograms were dominated by the signals of the internal standards, representing concentrations of 5 µg/L $^{13}C_6$-DEHA and 25 µg/L $^{2}H_4$-DEHP, respectively. The signal intensities of all other components detected were much lower. Method blank samples did not show any of the components reported in Table 3. These components are probably flavour components of the beverages originally bottled. Above a detection limit of approx. 1 µg/L, no further components could be detected.

Table 3: Tentative assignment of the components identified in water from PET bottles. Components listed in italic are present at levels very close to the detection limit (approx. 1 µg/L).

Bottle no.	Exposure	Age	Country of origin	Brand	Top	Sealing	Tentative assignment
1	Sun 60°C	used	Honduras	-	white	light blue	limonene *carvone*
2	Sun	used	Honduras	-	white	light blue	no components identified
3	Shade	used	Honduras	-	blue	clear	no components identified
4	Sun 60°C	new	Honduras	Coca Cola	red	light blue	myristicine limonene safrol *carvone* *terpinene*
5	Sun	new	Honduras	Coca Cola	red	light blue	myristicine limonene safrol *carvone* *terpinene*
6	Sun 60°C	used	Nepal	-	blue	without	no components identified
7	Sun	used	Nepal	-	blue	without	no components identified
8	Shade	used	Nepal	-	blue	without	no components identified
9	Sun 60°C	new	Nepal	Aqua Smile	blue	without	no components identified
10	Sun	new	Nepal	Aqua Smile	blue	without	no components identified
11	Sun 60°C	used	Switzerland	Migros	yellow	light blue	no components identified
12	Sun	used	Switzerland	Migros	yellow	light blue	no components identified
13	Shade	used	Switzerland	Migros	yellow	light blue	no components identified
14	Sun 60°C	new	Switzerland	Migros	yellow	light blue	no components identified
15	Sun	new	Switzerland	Migros	yellow	light blue	no components identified

3.2 Concentrations of DEHA and DEHP

The results of the migration experiments are compiled in Table 4. The table shows that DEHA and DEHP levels detected in water exposed in PET bottles are in the range of background levels as detected in pure water stored in glass bottles (volumetric flasks, volume 1 L) without any previous contact with PET. These levels are due to the ubiquitous presence of traces of these plasticizers. Therefore, the concentrations detected in the water from the PET bottles have to be taken as maximum levels; the contribution of migration of plasticizers to the background contamination is not significant.

Table 4: Levels and amounts of DEHA and DEHP in water from PET bottles.

Bottle no.	Exposure	Age	Country of origin	DEHA [µg/L]	DEHP [µg/L]	DEHA [µg/bottle]	DEHP [µg/bottle]
1	Sun 60°C	used	Honduras	0.046	0.33	0.091	0.66
2	Sun	used	Honduras	0.025	0.29	0.046	0.55
3	Shade	used	Honduras	0.024	0.19	0.034	0.28
4	Sun 60°C	new	Honduras	0.044	0.35	0.087	0.70
5	Sun	new	Honduras	0.023	0.31	0.048	0.64
6	Sun 60°C	used	Nepal	0.022	0.44	0.019	0.39
7	Sun	used	Nepal	0.016	0.18	0.015	0.18
8	Shade	used	Nepal	0.015	0.24	0.015	0.24
9	Sun 60°C	new	Nepal	0.012	0.71	0.012	0.70
10	Sun	new	Nepal	0.016	0.38	0.016	0.36
11	Sun 60°C	used	Switzerland	0.017	0.15	0.018	0.16
12	Sun	used	Switzerland	0.021	0.30	0.023	0.32
13	Shade	used	Switzerland	0.021	0.14	0.022	0.15
14	Sun 60°C	new	Switzerland	0.021	0.16	0.022	0.17
15	Sun	new	Switzerland	0.010	0.10	0.011	0.11
Blank 1	-	-	-	0.015	0.024	-	-
Blank 2	-	-	-	0.021	0.14	-	-
Blank 3	-	-	-	0.017	0.18	-	-

Comparison of the results can be based on the following criteria (see Table 5):

Exposure: The average levels of DEHA and DEHP in water from bottles exposed to sunlight and heated to 60°C are slightly elevated in comparison to the bottles exposed to sunlight without additional heating and to the bottles kept in the shade. No significant difference is seen between exposure to sunlight at ambient temperature and keeping in the shade.

Age: No significant difference can be observed between new and used bottles.

Country of Origin: DEHA levels in water from Honduras bottles are slightly higher than the levels in the remaining samples. No differences were found for the respective DEHP levels.

Table 5: Average and standard deviations of DEHA and DEHP concentrations grouped according to exposure, age, and country of origin of the PET bottles (see also Tables 1 and 4).

		DEHA [µg/L]	DEHP [µg/L]	DEHA [µg/bottle]	DEHP [µg/bottle]
Exposure:					
Sun 60°C	average	0.027	0.36	0.042	0.46
	standard deviation	0.014	0.21	0.037	0.26
Sun	average	0.019	0.26	0.027	0.36
	standard deviation	0.0054	0.10	0.016	0.20
Shade	average	0.020	0.19	0.024	0.22
	standard deviation	0.0045	0.053	0.010	0.067
Age:					
new	average	0.021	0.34	0.033	0.45
	standard deviation	0.012	0.22	0.030	0.27
used	average	0.023	0.25	0.032	0.32
	standard deviation	0.0092	0.10	0.025	0.18
Country of origin:					
Honduras	average	0.032	0.29	0.061	0.56
	standard deviation	0.011	0.062	0.026	0.17
Nepal	average	0.016	0.39	0.015	0.37
	standard deviation	0.0036	0.21	0.0026	0.20
Switzerland	average	0.018	0.17	0.019	0.18
	standard deviation	0.0046	0.074	0.0050	0.08
Blank:					
	average	0.018	0.11	-	-
	standard deviation	0.0032	0.031	-	-

3.3 Toxicological assessment of DEHA and DEHP concentrations

Toxicological assessment of the results is based on toxicological data for chronic exposure to DEHA and DEHP given in Table 6 [2-5]. These data are based on a daily *per capita* consumption of 2 litres of drinking water by a person weighing 60 kg. The assessment presented below represents a worst case situation as it is based on maximum detected DEHA and DEHP levels which are in the range of analytical background concentrations of these compounds.

Table 6: Carcinogenic risk from oral exposure to DEHA and DEHP (EPA Integrated Risk Information System [2, 3]) and WHO Guidelines values for drinking water quality [4, 5].

	Drinking water unit risk per µg/L	WHO Guideline value [µg/L]
DEHA	$3.4 \cdot 10^{-8}$	80
DEHP	$4.0 \cdot 10^{-7}$	8

The carcinogenic risk and the exploitation of the WHO guideline values resulting from maximum detected DEHA and DEHP levels are given in Table 7. Comparison of levels and toxicological data of DEHA and DEHP indicates a more critical situation for DEHP. Nevertheless, the levels of DEHP are still below a carcinogenic risk level of 1 in 10^6 and below the WHO guideline value for drinking water.

Table 7: Carcinogenic risk and exploitation of WHO guideline values resulting from permanent consumption of water contaminated with maximum detected levels of DEHA and DEHP after migration from PET bottles exposed to sunlight (see Table 4).

	Maximum concentration [µg/L]	Carcinogenic risk	Exploitation of WHO Guideline value
DEHA	0.046	$1.6 \cdot 10^{-9}$	$5.8 \cdot 10^{-4}$
DEHP	0.71	$2.8 \cdot 10^{-7}$	$8.9 \cdot 10^{-2}$

3.4 Summary and conclusions

Under conditions of solar disinfection of drinking water, migration of organic components from polyethylene terephthalate (PET) bottles to the water was studied. 6 bottles were exposed to sunlight at 60°C. For comparison, 6 bottles were exposed to sunlight at ambient temperature (maximum water temperature 34°C) and 3 bottles were kept in the shade at room temperature (25°C), respectively. Total time of exposure to sunlight was 17 hours. In order to elaborate the possible influence of further parameters, new and used bottles from different countries (Honduras, Nepal, and Switzerland) were selected.

Qualitative analyses of the water samples revealed traces of several organic compounds possibly due to flavour components of the originally bottled beverages. Above a detection limit of 1 µg/L, no further organic components could be detected.

Levels of the plasticizers di(2-ethylhexyl)adipate (DEHA) and di(2-ethylhexyl)phthalate (DEHP) detected in the water were 0.010 – 0.046 µg/L for DEHA and 0.10 – 0.71 µg/L for DEHP. As concentrations in blank samples were in a similar range (average 0.018 µg/L for DEHA and 0.11 µg/L for DEHP), the detected levels have to be considered as maximum levels. If the highest detected levels are used for a toxicological assessment of DEHA and DEHP (0.046 µg/L for DEHA and 0.71 µg/L for DEHP), the carcinogenic risk posed by permanent exposure to these levels is $1.6 \cdot 10^{-9}$ for DEHA and $2.8 \cdot 10^{-7}$ for DEHP, being below a carcinogenic risk of 1 in 10^6. Furthermore, these levels are distinctly below the WHO guidelines for drinking water quality (80 µg/L for DEHA and 8 µg/L for DEHP).

4 References

[1] D. Lilya, *Analysis and risk assessment of organic chemical migration from reused PET plastic bottles*, College of Graduate Studies, University of Idaho, Moscow, 2001.

[2] EPA Integrated Risk Information System, *Di(2-ethylhexyl)adipate (DEHP) (CASRN 103-23-1)*, U.S. Environmental Protection Agency, 1994, http://www.epa.gov/iris/subst/0420.htm.

[3] EPA Integrated Risk Information System, *Di(2-ethylhexyl)phthalate (DEHP) (CASRN 117-81-7)*, U.S. Environmental Protection Agency, 1993, http://www.epa.gov/iris/subst/0014.htm.

[4] WHO Guidelines for drinking water quality, *Di(2-ethylhexyl)adipate*, World Health Organization, Geneva, 1993, http://www.who.int/water_sanitation_health/GDWQ/Chemicals/di2ethylhexylsum.htm.

[5] WHO Guidelines for drinking water quality, *Di(2-ethylhexyl)phthalate*, World Health Organization, Geneva, 1993, http://www.who.int/water_sanitation_health/GDWQ/Chemicals/di2ethylhexyphtasum.htm.

Appendix

Figure 1: PET bottles are being filled with distilled water.

Figure 2: Test site on the roof of the Swiss Federal Institute for Materials Testing and Research.

Figure 3: Experimental set-up for sunlight exposure at 60°C.

Figure 4: Experimental set-up for sunlight exposure at 60°C.

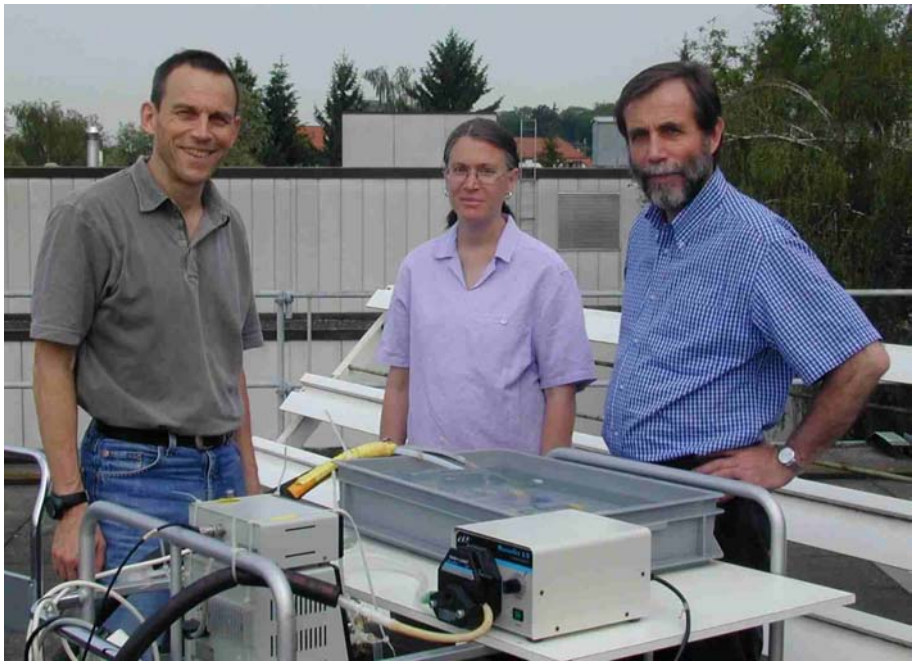

Figure 5: Detail of experimental set-up for sunlight exposure at 60°C.

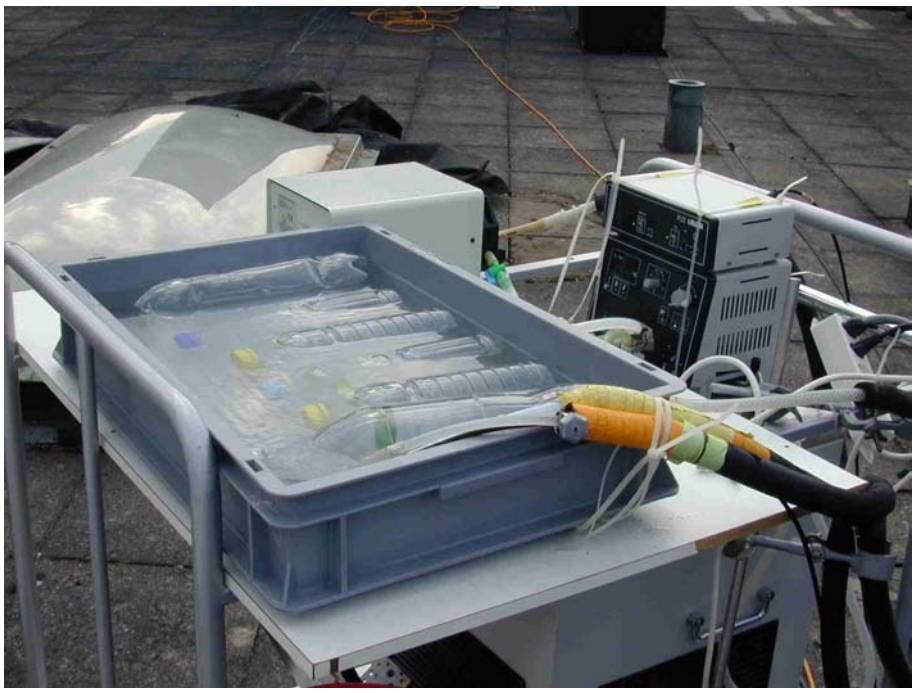

Figure 6: Detail of experimental set-up for sunlight at ambient temperature.