
Experimental Comparison of Chemical Migration from Petrochemical Plastic and Bioplastic Bottles into Drinking Water



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Contractor's Report

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Executive Summary

The chemical migration study described in this report was initiated by the California Department of Toxic Substances Control (DTSC), pursuant to an interagency agreement with the Department of Resources Recycling and Recovery (CalRecycle), and conducted in collaboration with Lawrence Berkeley National Laboratory and the University of California, Berkeley. One of the components of the DTSC/CalRecycle interagency agreement was to identify types of ingredients (chemicals and additives) used to manufacture bioplastic and petrochemical plastic water bottles, and to describe potential risks to human health related to the migration of these ingredients into drinking water.

Currently, information is limited on both the types of chemical compounds that are used in plastic bottle manufacturing processes and the potential for migration of those compounds into stored water. Further, data on a number of compounds measured in bottled water do not have sufficient toxicological data to support a hazard or risk assessment. Although this study resulted in the identification and measurement of a number of compounds in water, stored in plastic bottles under different conditions, none of the concentrations and chemicals indicated an immediate concern for public health.

There are three materials that are either currently used or may be used for single-use water bottles. These include polyethylene terephthalate (PET), which typically is a petrochemical plastic that is widely used in the beverage bottle industry, and two bioplastic polyesters including polylactide (PLA) and polyhydroxyalkanoate (PHA), which are plastics produced through fermentation. Some PET bottles are made from bio-based materials, but they are not included in this report.

Information is limited on chemical compounds that are used in the water bottle industry and the potential for migration of those compounds into water stored in PET or PLA. Commercially produced PHA water bottles were not readily available for this study. A finite number of plastic water bottle samples were tested in this study and thus only give a limited view of the bottles and manufacturing processes used by industry. This study yielded results for specific bottles produced at a certain point in time and does not purport to capture all chemicals that can potentially migrate into water.

The approach used in this study was to first identify potential target compounds through a literature review and second, to identify compounds in the plastic bottle matrixes (PET and PLA) by experimentally using direct thermal desorption gas chromatography, mass spectroscopy. The list of target compounds was reduced to include chemicals that could migrate into water using a hot water extraction approach and a high volume stir-bar sorptive extraction approach.

The final list of target compounds was tracked and quantified for different storage times and temperatures in composite samples representing seven different bottle types and manufacturers including one commercially filled PET bottle, three different manufacturers of fully blown never-filled PET bottles and three different fully blown never-filled PLA bottles (from two manufacturers). A third screening was conducted at the end of the storage experiment to confirm the presence of compounds in the water samples. The quantified chemicals were prioritized with respect to potential human health hazard and a preliminary exposure assessment was conducted on a select number of compounds.

The literature review conducted in support of this work (Appendix A and Appendix B) and the review by Bach et al, (2012) concluded that measured chemical concentrations and bioassay results for water stored in PET and PLA, are inconclusive due to a lack of standardized testing methods. This study used three screening methods (direct thermal desorption, hot water extraction, and large volume water extraction) and three different analysis methods—thermal desorption gas chromatography mass spectrometry (TD-GCMS), inductively coupled plasma mass spectrometry (ICPMS), and high performance liquid chromatography mass spectrometry (LCMS)—to develop a list of target compounds relevant to water stored in PET and PLA. The final target list was then used to quantify chemical migration results during storage times including overnight, three months, and six months at $\sim 22\text{ C}^\circ$ ($\sim 71^\circ\text{F}$), 35 C° ($\sim 95^\circ\text{F}$), and 50 C° ($\sim 122^\circ\text{F}$).

During the storage experiment, the PLA bottles failed by disintegrating during the highest temperature storage condition; thus, data for PLA are only available at room temperature storage (22 C°) and storage at 35 C° . Although this event was not anticipated, PLA products are often designed and certified to be compostable (whereby degradation of plastic materials is initiated in compost environments at temperatures exceeding 45 C°). This design factor may have activated the bottles' deterioration. Data for the PET bottles, which were able to withstand the highest temperature tested (50 C°), was captured for all three storage scenarios.

Measured concentrations of target chemicals during the storage test ranged from about 10 parts per trillion (ppt) up to a few parts per billion (ppb) with many compounds showing a trend towards higher levels under both increasing temperatures and longer storage times. The overall average temperature effect (\pm the standard error of the mean, S.E.) for migration considering all compounds tested was a relative increase in concentration by a factor of $9.4 (\pm 2.9)$ for each 10 degree rise in storage temperature over six months of storage for PET. The same factor for PLA was $7.2 (\pm 2.5)$.

In other words, if the measured concentration of a compound in water stored in PET is 3 ppb when stored at 20 C° then the concentration of the same compound stored in the same bottle at 30 C° would be $3\text{ ppb} \times 9.4 = 28.2\text{ ppb}$. A small effect was seen for storage duration where the increase over three months of storage was by a factor of $3.8 (\pm 0.4)$ and $3.7 (\pm 0.6)$ on average for all chemicals tested for PET and PLA, respectively. Results for the elements measured during the storage experiment were somewhat less consistent but also generally showed an increasing trend in concentration with increasing storage time and temperature for elements that likely originate in the bottle matrix.

An uncertainty analysis and quality assurance measurements conducted during the study indicate good precision in all measurements. A few compounds, including mostly phthalates, had more variability across the different replicate measurements indicating that these compounds may not be associated with all water bottles and may be related to packaging or trace experimental contamination.

The quantified compounds were prioritized for preliminary hazard assessment based on their known or suspected toxicity, detection in significant concentrations during the storage experiment, and chemical relevance to plastic production. The final prioritized list included seven organic compounds and two elements.

The final prioritized list showing the maximum measured concentration for each compound over the storage experiment is provided in Table 8. Health hazard data related to the prioritized

compounds was reviewed and a screening level exposure assessment was conducted. The health hazard assessment relied on generalized assumptions for the exposure assessment including the average and upper 95th percentile intake rates for children (ages 1-2) and adults with all drinking water from bottles and the average exposure concentrations measured from the three-month storage at 30 C°.

Several of the substances on the prioritized list are known to be hazardous, including: benzophenone, a known carcinogen; and diisobutyl phthalate, a known endocrine disruptor affecting male reproductive development at low doses (see section on Hazard Assessment). There are no exposure limits in water (MCL) established for these substances. However, our preliminary analysis indicates that, under the conditions of this experiment, exposure would be too low to pose significant health risk, based on the toxicity information publicly available for these substances.

Although the findings of this experiment do not suggest an immediate health risk posed by chemicals leaching from PET or PLA water bottles, it is important to remain cognizant of the many gaps in toxicity data, limitations in the measured exposure concentration data, and the reality that people are exposed to many of these substances from multiple sources whose impacts can be cumulative. Therefore, even low level exposures, when known, can provide an opportunity to incrementally reduce exposures in the population.

Limitations in the data provided by this report include the fact that measurements were typically exceedingly low, which created challenges with analysis including interfering levels of background contaminants in the test water and trace contaminants introduced during the sample processing. Additionally, the LCMS data was not fully analyzed due to budgeting and time constraints, resulting in the possibility that trace high molecular weight and highly polar contaminants may be present but the preliminary review of the LCMS data did not reveal any potential target compounds.

Finally, the study only considered storage time and temperature and did not consider factors such as water/bottle treatment prior to and during filling or environmental factors such as direct sunlight or contaminants in the storage environment that may diffuse into bottled water over time.

Table 1 Maximum measured concentrations for prioritized chemicals.

Name	CAS#	Maximum concentration	
		µg/L	Sample
Diisobutyl phthalate	84-69-5	0.482 ± 0.064	PLA-Fc T2S2
Benzophenone	119-61-9	1.280 ± 0.076	PET-A T3S2
Phenanthrene	85-01-8	0.318 ± 0.026	PET-A T3S2
2,2-Dimethoxy-1,2-diphenylethanone	24650-42-8	2.080 ± 0.258	PET-A T3S2
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	0.882 ± 0.130	PET-C T3S2
3,5-Di-tert-butylbenzoquinone	719-22-2	1.650 ± 0.074	PET-C T3S2
2,4-Di-tert-butylphenol	96-76-4	1.460 ± 0.286	PET-A T3S2
Tin (Sn)	7440-31-5	0.074 ± 0.008	PLA-Fg T1S1
Antimony (Sb)	7440-36-0	5.930 ± 0.44	PET-C T3S2

Future work should consider improving methods for screening water-borne contaminants in stored water. A method developed during this study using full water bottles and stir-bar extraction could be a useful for testing commercially filled bottles but would require additional development to optimize the method. In addition, it would be useful to develop a comprehensive database of contaminants found in bottled water and to further test both bottling and environmental factors that could contribute to migration of contaminants from bottle matrixes to stored drinking water. Finally, it is important to continue to build upon the toxicological data relevant to bottled water.

Project Background

The California Department of Toxic Substances Control (DTSC), pursuant to an interagency agreement with the Department of Resources Recycling and Recovery (CalRecycle), aims to reduce the environmental impacts of plastic container manufacturing, of plastic container recycling, and of plastic containers disposed in the environment. Through this interagency agreement, DTSC and CalRecycle support the resolution of the California Ocean Protection Council on Reducing and Preventing Marine Debris dated Feb. 8, 2007, which identifies and prioritizes solutions (one of which is to seek innovative methods to reduce plastic wastes).

One of the research components of the DTSC/CalRecycle interagency agreement is the identification of ingredients (additives and chemicals) found in plastic water bottles made from petrochemical plastics and bioplastics and to further understand the extent to which any additives identified in materials used in the production of water bottles might leach into beverages contained in them. This information would aid in the determination of the types of chemicals in different plastic containers and in determining the potential for human and/or ecological exposures.

There are three materials that are either currently used or may be used to produce water bottles. These include polyethylene terephthalate (PET), which typically is a petrochemical plastic widely

used in the beverage bottle industry, and two bio-based polyesters including polylactide (PLA) and polyhydroxyalkanoate (PHA), which are bioplastics produced through fermentation. Ahmed and Varshney (2011) have reviewed the potential for PLA to gain market share in the packaging industry while Keshavarz and Roy (2010) have reviewed the potential for PHA and issues related to production and application.

Publically available information about additives, copolymers, and catalysts used in the production of PET bottles is limited and almost no information is available for PLA or PHA bottles. Nor is there a body of information about potential migration of chemicals into the liquid contents of either bottle type. This lack of scientific research limits our ability to fully assess the tradeoffs between petrochemical and bio-based plastics and to estimate the potential life cycle impacts of plastic materials.

The primary focus of this study is identification and quantification of contaminants that leach into drinking water stored in beverage containers. Although both PLA and PHA have potential for gaining market share in the water container industry, at the time of this study only PLA bottles were available in fully blown never-filled form while PHA was only available as pre-forms. Therefore, only PET and PLA bottles were fully characterized during this study. The PHA material, available only as pre-forms, was included in an initial screening experiment (using direct thermal desorption of the plastic material) but not included in the storage phase of the study.

In the execution of this study, a systematic approach was used to identify chemicals that are found in PET and PLA and then to assess the migration of chemicals from the plastic beverage containers into drinking water stored in them. Chemicals typically present in the plastic matrix were first identified through a literature review, then confirmed experimentally by a direct thermal desorption gas chromatography, mass spectroscopy approach. The list of target compounds was then focused on chemicals that could migrate into water using a hot water extraction approach and finally through a high volume stir-bar sorptive extraction step.

The final list of target compounds was tracked and quantified for different storage times and temperatures in seven bottle types including one commercially filled PET bottle, three different manufacturers of fully blown never-filled PET bottles, and three different manufacturers of fully blown never-filled PLA bottles. The quantified chemicals were prioritized with respect to potential hazard to human health and a preliminary exposure assessment was conducted on a select number of these compounds.

Introduction

The International Bottled Water Association reported that in 2010, there was a 3.5 percent increase in total bottled water consumption in the United States (Beverage Marketing Corporation, 2011). With continuing demand for bottled water comes a growing concern about the amount of plastic in the waste stream (Sinha et al, 2010). In 2009, the U.S. Environmental Protection Agency (U.S. EPA, 2010) estimated that approximately 30 million tons of plastic waste was generated in the U.S., and of that, only 7 percent was estimated to be recycled. Currently, the most commonly used plastic for bottling drinking water is polyethylene terephthalate (PET), and due to its high use, there is consumer interest in knowing if there are chemicals that may leach from the bottle into drinking water. However, the introduction of

biodegradable plastic could potentially result in new chemical constituents and additives in the product stream with the potential for migration into drinking water and/or the environment.

Though bottled drinking water safety and quality is regulated at the federal, state, and industry levels, publicly available data is limited on the chemical composition and chemical migration potential for petrochemical-based plastics like PET. Data is even sparser for bio-based plastics like PLA and PHA. Bach et al., (2012), provide a detailed review of organic chemicals reported in water contained in PET along with a review of toxicological results from bioassays conducted on the water. They concluded the wide range of chemical analytical methods and test conditions have led to contradictory results related to both the chemical migration from PET and the measured toxicity based on bioassays.

Contaminants found in water stored in PET can originate from a variety of sources. The three primary sources of contaminants in bottled water include the source aquifer for the water, contaminants associated with the bottling process, and contaminants that leach from the bottle plastic or cap into the water (Diduch et al., 2012).

There are very few available publications reporting organic chemicals in water stored in PLA bottles. Studies of PLA sheets that considered the migration of lactic acid and the hydrolysis of similar compounds into lactic acid during food storage in PLA material concluded that the migration of lactic acid and its derivatives was limited (Conn et al., 1995; Mutsuga et al., 2008). Lactic acid is considered a generally recognized as safe (GRAS) food additive by the Food and Drug Administration (21CFR184.1061) so is likely of low concern as a migrant from plastic into stored water.

Concentrations of major and trace elements have been summarized for 132 bottles (mostly PET) collected internationally (Krachler and Shotyk, 2009). The dependence of concentration on storage conditions (Shotyk and Krachler, 2007), temperature (Reimann et al., 2012), treatment process for reused bottles (Andra et al., 2011), and composition of bottle contents (Reiman et al., 2010) have also been reported for PET. The primary elemental contaminant that has been identified to leach from PET is antimony (Sb) (Reimann et al., 2012). No information is available for the migration of elements from PLA into water.

The objective of this project was to identify chemicals in fully blown never-filled plastic water bottles, obtained from several different manufacturers, and to determine whether those chemicals migrated from the bottles into drinking water under different storage scenarios. For those chemicals that were identified and quantified in the water, a screening level exposure assessment was conducted and results were compared to published toxicity data.

Methods

Literature review

Target chemicals

In addition to the references included in the body of this report, a literature review was conducted prior to and during the initial stages of this project. Both published papers and unpublished documents and websites were reviewed. The research performed to identify chemicals that have

been measured in PET or in water stored in PET is summarized in Appendix A. A number of additional sources were consulted to identify chemicals associated with all three plastics (PET, PLA, and PHA) used to produce water bottles. These compounds are potential candidates for migration from plastic to water and are provided in Appendix B. Compounds associated with PET are listed in Table A. 3 and in Table A. 4. Chemicals used in the production of PLA and PHA are summarized in Table A. 5 and Table A. 6, respectively.

The literature review revealed more than 300 compounds potentially used in the production of PLA, PHA, and PET representing a wide range of chemical and elemental classes. However, other than a few compounds used in plastic production processes that are known to migrate into water under certain conditions (i.e., antimony), there is no consistent and reliable list of ingredients used to make bottles. Therefore, it was important to design a study of chemical migration with a sufficient variety of analytical methods capable of detecting the range of chemical classes that can potentially migrate from bottles into water.

Chemical sampling and analysis methods and assays

A wide range of sampling and analysis methods are available for detecting and measuring substances in water, as summarized by Madrid & Zayas (2007). One of the most common methods used for sampling and analysis of water for organic compounds is liquid-liquid extraction (LLE) followed by gas chromatography/mass spectrometry (GC/MS) (Loschner et al., 2011; Leivadara et al., 2008; Kohler & Wolfensberger, 2003; Diana & Dimitra, 2011; Bosnir et al., 2007; Schmid et al., 2008).

Because LLE requires the concentration of large volume solvent extracts prior to analysis, it is not appropriate for volatile range compounds that can be lost during concentration steps. Purge and trap methods with GC/MS analysis are often used to sample volatile contaminants in water (Skjervrak et al., 2005; Leivadara et al., 2008) by collecting chemicals purged from the water in bubbling air that is passed through a sorbent material. This step is followed by thermal desorption GC/MS analysis.

Another common approach to identify low volatility VOCs and semi-volatile organic chemicals is solid phase extraction where water is passed through a cartridge containing a sorbent then extracted with solvent that is concentrated and analyzed by GC/MS (Skjervrak et al., 2005). Large molecular weight and/or highly polar compounds that are not amenable to analysis by GC/MS are often analyzed by liquid chromatography/mass spectroscopy (LC/MS) (Milon, 1991; Nasser et al., 2005; Buchalla & Begley, 2006; Bentayeb et al., 2007) using direct analysis of the water or after a pre-concentration step.

The LLE and the solid phase extraction methods both require a significant amount of solvent that must be concentrated prior to analysis. Solid-phase microextraction (SPME) of head space samples has been used to measure volatile compounds directly from water (Cho et al., 2003; Simoes et al., 2007) reducing the need for solvents. SPME was used in an experiment to measure phthalates associated with the genotoxicity of water packaged in PET bottles but the concentrations were below detection limits (Ceretti et al., 2010).

The detection limits for SPME depends on the capacity of the thin sorbent fibers used. An approach with a higher capacity for detecting contaminants that can be used directly in water samples is the stir-bar sorptive extraction (SBSE) method. SBSE uses the same principle as SPME but uses a thicker sorbent film and longer contact time that increases sampling capacity for

VOCs (Tienpont 2006; Prieto et al., 2007). The stir bar can be analyzed directly by thermal desorption GCMS (Kawaguchi et al., 2008) or by solvent extraction (Serodio & Nogueira, 2004) followed by GCMS or LCMS. The SBSE methods have detection limits ranging from 1 µg/L for VOCs to sub-ng/L for LV-VOCs and SVOCs including a wide range of water-borne contaminants (David et al., 2003).

The study of chemical elements in water typically uses water sampled directly from bottles and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Reimann et al., 2012; Reimann et al., 2010; Andra et al, 2011; Krachler & Shotyk, 2009; Cheng et al, 2010; Westerhoff et al., 2008; Keresztes et al., 2009; Hansen & Pergantis, 2006; Andra et al., 2012; Peh et al., 2010; Shotyk & Krachler, 2007). The primary element associated with PET is antimony although several other elements are listed as possibly being used in the manufacture of PET, including cadmium, cobalt, germanium, lead, manganese, silver, titanium, and zinc (Table A. 3).

No information is available about elements that might leach from PLA into water although a number of elements are listed as possibly being used in the production of PLA, including alkoxides and oxides of magnesium, aluminum, magnesium, tin, titanium, zinc, and zirconium (Table A. 5).

A variety of bioassays have been conducted to identify toxicity of water stored in PET bottles. These assays include tests of estrogenic activity (Pinto & Reali, 2009; Wagner & Oehlmann, 2009), genotoxicity (Ceretti et al., 2010) and carcinogenicity/mutagenicity (De Fusco et al., 1990; Biscardi et al., 2003). These studies have been summarized by Bach et al, (2012) along with associated chemical assay data and the results show an increase in mutagenicity with storage and exposure to light (De Fusco et al., 1990) but overall the results were not consistent. The inconsistency may be due to the lack of a standardized protocol for testing water bottles either for chemical migration or for toxicity (Bach et al., 2012).

To provide the largest range of chemical classes for the water analysis in this study, three sampling and analysis methods were selected: 1) the stir-bar sorptive extraction GC/MS method to analyze for a broad range of VOCs, low volatility VOCs (LV-VOC), and semi-volatile organic compounds (SVOC) extracted directly from water; 2) the LC-MS method to analyze polar and high molecular weight compounds and oligomers directly from water; and 3) the ICP-MS method to analyze the full range of elements sampled directly from water.

Experimental Design

A detailed overview of the experiments conducted in this study, including the specific steps taken, is provided in the subsequent sections. In addition to the formal storage experiment conducted at different temperatures and for different storage durations, the study included several screening level experiments designed to systematically identify chemicals in the polymer matrix, those chemicals that could potentially leach into water, and to confirm the chemicals actually measured during the storage experiment.

Screening experiments to identify target chemicals

Three different screening level experiments were conducted. The first used direct thermal desorption of small polymer samples from each manufacturer and plastic type to identify chemicals in the bottle matrix that could be volatilized from the polymer by direct thermal desorption (Zweiben & Shaw, 2009). This screening experiment, which was used primarily to

detect a range of volatile organic compounds, resulted in a list of 49 compounds found in the polymer matrix. The results from the direct thermal extraction did not provide information about potential migration from plastic into water.

To begin to address the potential for migration, a second screening experiment was conducted. This method created aggressive water extraction conditions by elevating temperature and pressure with an accelerated solvent extraction (ASE) system to simulate a worst-case condition for leaching by water. This experiment enabled the identification of chemicals that could potentially leach into water. The results from the ASE extraction were added to the preliminary target list from the direct thermal desorption screening.

To narrow down the target list, a final screening level experiment was conducted after the completion of the storage experiment (described below). Working at the ultra-trace levels required by the water extractions presented the added challenge of differentiating target compounds from background contaminants in the lab and analytical procedures. To limit the chance for contamination and lower detection limits even further, the third screening experiment included stir-bar sorptive extractions performed directly with the water in the filled bottles. The screening confirmed the findings of low level contaminants during the storage experiment and was used to finalize the list of target compounds.

No internal standard or calibration was used during the screening experiments so all three experiments were used primarily for qualitative identification of target compounds, but an added outcome from the series of screening experiments was to confirm the low level measurements made during the actual storage experiments.

The series of screening experiments provided data to systematically identify target chemicals that were in the polymer matrix and of those present in the matrix, to identify and confirm the chemicals that have potential to migrate into the water.

Storage experiment

LBNL received test bottles representing six different combinations of suppliers and material types for the never-filled bottles, plus one commercially filled bottle type. A schematic of the experimental design is shown in Figure 1. Each of the manufacturer and material sets consisted of 21 bottles with caps from a given production batch. The bottles were divided into seven treatments consisting of three bottles each. Three bottles were used to prepare a composite of multiple bottles prior to analysis given that we lacked initial information about variability for individual manufacture/bottle types.

For the commercially filled water bottles, LBNL received several cases from one manufacturer for testing. As with the never-filled bottles, the commercially filled bottles were combined in sets of three bottles for each sample and included in the three- and six-month storage experiment. The fill date commercially filled bottles was not available so an initial sample represented the start of the storage experiment rather than the overnight storage scenario. Never-filled fully formed PET and PLA bottles were available for testing but PHA bottles were only available as pre-forms. Therefore, the PHA was only included in the initial testing using direct thermal desorption. The PET, PLA, and commercially filled PET bottles were included in all screening and storage experiments.

At initiation of the experiment, bottles were rinsed three times with warm carbon filtered tap water (Aqua-Pure, model SST-1) and then the rinsed bottles were filled and capped with the warm carbon filtered tap water. An aliquot of fill water was collected in a glass bottle for use in determining background contaminants in the fill water. One set of test bottles was stored at room temperature overnight (~ 12 hours) then sampled for analysis (details on sampling and analysis method provided below). Two of the filled sets of bottles were placed in each of three different temperature controlled environments (~22°C, 35°C and 50°C) in the dark to test storage/temperature effects.

At three months, one set of bottles from each temperature regime was harvested and the water contained in the bottles was sampled and analyzed. At six months the remaining set of bottles was harvested, sampled and analyzed. Blank water was prepared at the time of filling and stored in rinsed amber bottle that previously contained HPLC grade water.

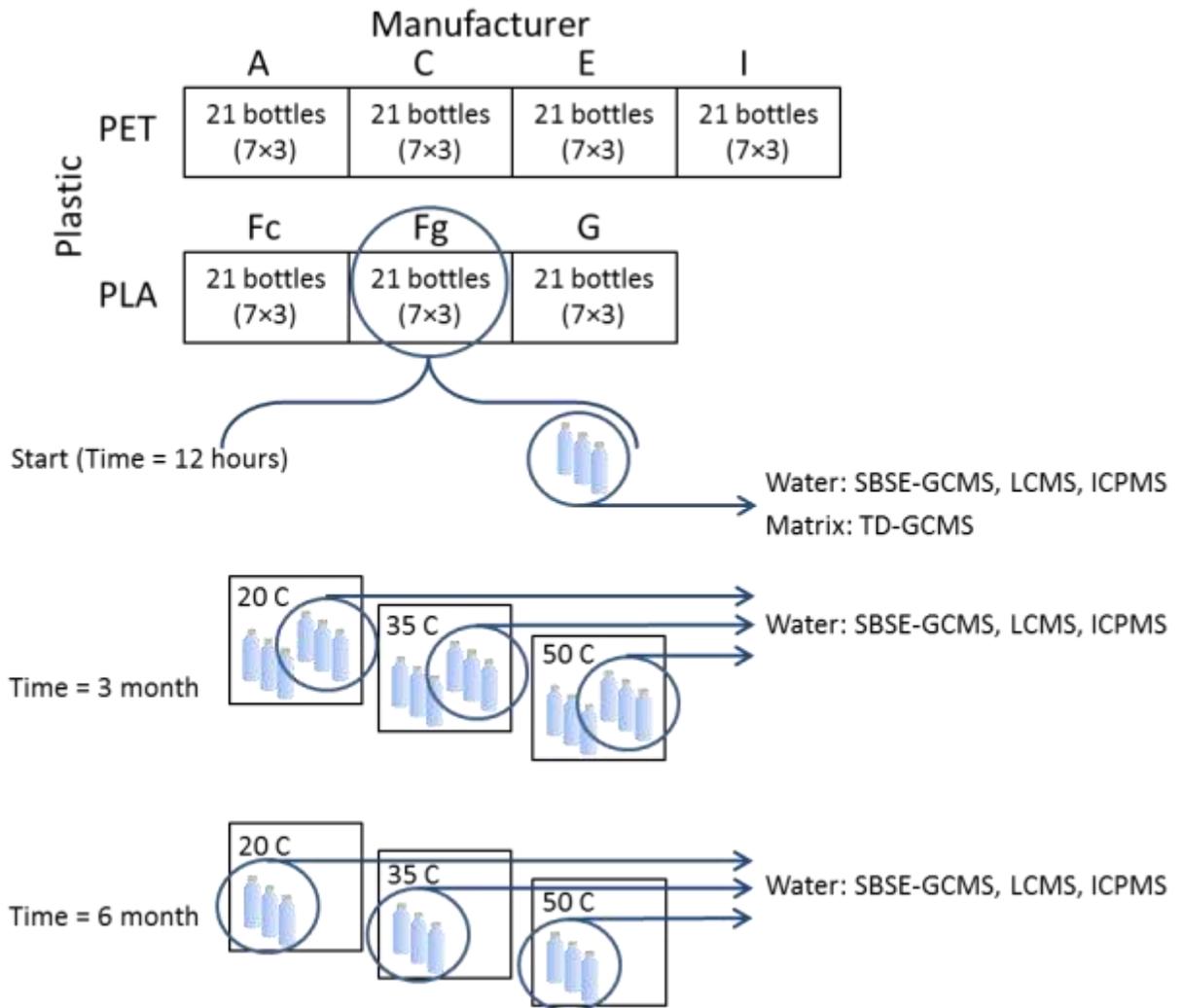


Figure 1. Schematic showing the full experimental design for plastic type (PET and PLA) and manufacturer (identified by letter) with an expanded view of one combination showing the plan for sampling seven treatments for each composite set (three bottles) of containers measured at three storage times (overnight, three-month and six-month) and three storage temperatures (room temp, 35 C° and 50 C°). The start time sampling includes one composite set stored overnight at room temperature. The screening experiments are not shown in the experimental matrix.

Identification and Acquisition of Bottles for Testing

Eighteen bottle manufacturers and water bottle companies in California were identified by DTSC and UCB. Sources of never-filled, fully blown water bottles (with caps) were identified from the list and contacted by UCB and/or DTSC. The required number of bottles from each supplier and material were either purchased from or donated by the companies. Bottles were received in a variety of packaging ranging from loose plastic bags to boxes with and without packing material

(foam peanuts). Bottles were stored as received at room temperature until use. In addition to the never-filled, fully blown PET and PLA bottles, a limited number of pre-form PHA bottles were obtained. Finally, two cases of commercially filled water bottles were purchased off-the-shelf for testing. All bottle manufacture/type combinations were coded with a letter by UCB before delivery to LBNL. Identification of manufacturer and bottle type related to each code was provided to CalRecycle but are not included in this report.

Identification of Chemicals

The selection of target compounds for this study was based on 1) a literature review performed by DTSC focused on identifying previously reported additives and/or contaminants in each of the plastic types (Appendices A and B), 2) a review performed by UCB of toxicological data related to additives and/or contaminants identified by DTSC, 3) input provided by LBNL of analytical methods and existing analytical capabilities for the different classes of chemicals that may be present in the water bottles and contents, and 4) a series of screening measurements performed on the plastic matrix and water using different extraction techniques including direct thermal desorption, hot water extraction, high pressure liquid extraction, and large volume stir-bar sorptive extraction.

The preliminary list of target compounds was used to guide the development of chemical sampling and analyses methods for this study. Beyond the initial target compounds, a large number of initially unidentified contaminants were encountered during the screening experiments. When the response for these unidentified contaminants was high enough (i.e., signal-to-noise ratio greater than 10) then the compounds were tentatively identified where possible by library search using the National Institute of Standards and Testing (NIST) mass spectral search program for the NIST/EPA/NIH mass spectral library (version 2.0d build April 26, 2005) and by spectral deconvolution using the NIST Automated Mass Spectral Deconvolution and Identification System (AMDIS) in combination with the NIST mass spectral library. If a unique identification was not found with the library search then the compound was labeled by retention time in the analysis and chemical class (i.e., 52.583, unknown alkyl phenol).

Materials

Chromatography, Pesticide Residue Analysis, and Spectrophotometry-grade methanol (Burdick & Jackson, Muskegon, MI) were used in this study. An internal standard was prepared using D₄-dimethyl phthalate (AccuStandard, New Haven, CT). The stir-bar extractions were carried out on 10 mm long magnetic stir bars (Gerstel, Mulheim a/d Ruhr, Germany) coated with a 0.5 mm layer of polydimethylsiloxane (PDMS). Before use, the stir-bars were conditioned in thermal desorption tubes (TDT) at 300 °C for 2 hours in a tube conditioning oven (Gerstel, model TC2) under a flow of Helium at a rate of 70 mL/min. Stirring was conducted on a 20 position magnetic stirrer (Gerstel). Never-filled preformed bottles were obtained directly from various bottlers and bottle manufacturers. Three types of PLA plastic bottles were obtained from two different manufacturers, as well as three different types of PET bottles and one commercially filled PET bottle. An Aqua-Pure SST1/SST1HA Carbon filter (3M, St. Paul, MN) was used to filter tap water for the samples.

Sample collection and preparation

Direct Thermal Desorption

The samples for direct thermal desorption were cut from unlabeled never-filled bottles into small pieces (~ 2 – 5 mm) for a total of 3.5 g. The pieces were installed in the heated zone of an empty thermal desorption tube and held in place with pre-cleaned glass wool (confirmed clean by GC-MS analysis prior to use). The samples were analyzed immediately following preparation.

Aqueous phase analysis

On the day of analysis after the predetermined storage period (overnight, three-month, 6-month), a 50 mL aliquot of water with one-third from each of the three bottles in each composite sample was transferred to a 60 mL glass vial and sealed with a Teflon lined cap. Multiple composite samples were prepared for each composite sample to allow for the three different analytical methods and some extra test materials for replicate quality assurance analyses. Blank samples were prepared by filling the same size vials with carbon filtered tap water.

Stir-bar sorptive extraction sample prep: The composite water samples (50 mL) were spiked with 5 mL of deuterated internal standard solution (2 ng/mL D₄-dimethyl phthalate in methanol) and extracted using stir-bar sorptive extraction (SBSE). Twisters™ (Gerstel, Mulheim a/d Ruhr, Germany). The SBSE was conducted for four hours at 2,000 revolutions per minute (rpm). After extraction, the stir bars were removed from the sample solutions using a Kimwipe covered magnet and rinsed with filtered tap water, dried on a clean and lint-free paper to remove residual water and particulates, and placed in a dedicated thermal desorption tube for analysis. The thermal desorption tube containing the stir-bar was stored in a polymer sleeve with the glass tube sealed between two Teflon lined caps.

ICP-MS sample prep: Water from the composite samples was poured into polypropylene tubes that were pre-cleaned following the procedure outlined in ASTM D4453-11 Standard Practice for Handling of High Purity Water Samples. From these samples, an aliquot was removed and spiked with an internal standard to 20 ug/L (6Li, 45Sc, 71Ga, 103Rh and 169Tm). The spiked samples were analyzed immediately following preparation.

LC-MS sample prep: Water from the composite samples was spiked with 5 ml of deuterated internal standard (2 ng/mL D₄-dimethyl phthalate in methanol) then transferred to 200 ml concentration vial (TurboVap II configured for 200 ml vials) along with two 5 ml MeOH rinses of the composite sample vial. Samples were concentrated to 2.5 ml under N₂ and transferred to a 5 ml Teflon capped amber vial along with 2.5 ml high performance liquid chromatography (HPLC) grade water that was used to rinse the TurboVap tube resulting in a final volume of aqueous sample of 5 mL. An aliquot of the concentration aqueous sample was transferred to an auto-sample vial for analysis by LC-MS.

Instrumentation

GC-MS analysis

The direct thermal desorption method and the stir-bar sorptive extraction method both used similar GC-MS analysis conditions with slight differences in the desorption conditions. The conditions for desorption are described first for both method followed by the common GC-MS conditions.

Both direct thermal desorption and stir-bar sorptive extraction samples were thermally desorbed for analysis by gas chromatography/mass spectrometry (TD-GC/MS) using a thermodesorption auto-sampler (Model TDSA2; Gerstel), a thermodesorption oven (Model TDS3, Gerstel), and a cooled injection system (Model CIS4; Gerstel). The cooled injection system was fitted with a Tenax-packed glass liner (P/N 013247-005-00; Gerstel). Desorption temperatures of 25 °C with a 0.5-minute delay followed by a 60 °C/min ramp to 300 °C and a 4-minute hold time for the SBSE or to 100 °C with a 10-minute hold time for direct thermal extraction were used. The cryogenic trap is held at 1 °C for the SBSE during thermal desorption, then heated within 0.2 minutes to 290 °C at a rate of 12 °C/s, followed by a 2-minute hold time. For the direct thermal desorption, the cryogenic trap was held at -40 °C during thermal desorption, then heated within 0.2 minutes to 280 °C at a rate of 12 °C/s, followed by a 3.5-minute hold time.

Once desorbed, the analytes from both methods were resolved on a GC (Series 6890Plus; Agilent Technologies) equipped with a 30 meter HP-1701 14% Cyanopropyl Phenyl Methyl column (Model 19091U-233; Agilent Technologies) at an initial temperature of 10 °C for 2 minutes, then ramped to 40 °C at 5 °C/min, to 140 °C at 3 °C/min and finally to 280 °C at 10 °C/min, holding for 10 minutes. The resolved analytes were detected using an electron impact MS system (5973; Agilent Technologies). The MS was operated in scan mode. Multipoint calibrations were prepared from standard set of pure compounds representing a range of chemical classes. The calibration was prepared by spiking known amount of pure standard in 50 mL of filtered water and extracted/analyzed as regular samples. The calibration was prepared for the total ion current and an average response ratio was derived for all compounds and used to quantify all target compounds. All pure standards and analytes were referenced to an internal standard (~10 ng) of D₄-dimethyl phthalate.

ICP-MS analysis

Elemental analysis was carried out on Perkin Elmer SCIEX Elan DRCII dynamic reaction cell quadrupole ICP-MS using a quantitative method (six standards). Ammonia (0.4 mL/min) was used as a reaction gas when analyzing for K, Ca, V, Cr, Mn, Fe and Se to remove interferences and thus lowering detection limits.

LC-MS analysis

Concentrated aqueous samples were analyzed on an Agilent 1200 series liquid chromatograph (Santa Clara, CA) connected in-line with an LTQ Orbitrap XL hybrid MS equipped with an Ion Max electrospray ionization source (ESI; Thermo Fischer Scientific). The LC was fitted with a Pinnacle DB Aqueous C18 reverse phase column, 100 mm by 1 mm ID with 4 µm particle size (Restek) and associated guard column. The mobile phase was MeOH-H₂O (85:15 v/v).

Results

Direct thermal desorption screening experiment

The direct thermal desorption screening analysis was conducted three times in series for each of the PLA manufactured bottles and for one of the never-filled PET bottles. The resulting mass spectra were used to identify possible target compounds in the plastic matrix using the NIST mass spectral search program for the NIST/EPA/NIH mass spectral library (version 2.0d build April 26, 2005) and by spectral deconvolution using the NIST Automated Mass Spectral Deconvolution

and Identification System (AMDIS) in combination with the NIST mass spectral library. Forty-nine compounds were tentatively identified in the PLA and/or the PET plastic. Plastic from a PHA preform bottle was also included in the direct thermal desorption analysis and a significant number of compounds across a wide range of volatilities and chemical classes were tentatively identified. Given the significant difference in direct thermal desorption results for the PHA preforms relative to the fully blown never-filled bottles of PET and PLA, it was concluded that the PHA results were not relevant to fully blown bottles and/or chemical migration tests. Therefore, the PHA results are not reported and PHA was excluded from further testing.

The 49 tentatively identified compounds from the direct thermal desorption of PET and PLA are shown in Figure 2 along with the relative mass in each plastic matrix (across top axis) and the total amount measured from the three consecutive direct thermal desorption cycles (across bottom axis) for each matrix. The mass for each compound is reported as the toluene equivalent mass. The toluene equivalent mass is calculated from total ion current from the analysis and the relative response factor for toluene (ng toluene per unit area of peak). The relative amount in the two plastic matrix types is calculated as the total mass from the three desorption cycles for PET divided by the average of the total mass from the three different PLA bottles normalized to a value between one (all mass in PET) and zero (all mass in PLA). The results from the direct thermal desorption experiment show that the majority of compounds are associated with the PLA matrix but the absolute values are relatively low. The maximum value measured during the direct thermal desorption was for 1,4-Dioxane-2,5-dione,3,6-dimethyl-, which is lactide or a cyclic dimer of lactic acid. The lactide was measured at ~ 200 ng total for three desorption cycles from ~grams of matrix in PLA.

Chemical Identification

The results from the direct thermal desorption include chemicals that volatilize from the plastic matrix at temperatures $\leq 100\text{ C}^\circ$ and products of thermal decomposition. Although the direct thermal desorption provides an initial indication of the presence of compounds in the plastic matrix, it does not demonstrate potential for migration into water during storage. To build on the initial list of target compounds and to identify those compounds that could potentially migrate from the matrix into water, two additional water-based screening experiments were conducted.

The first was an Accelerated Solvent Extraction experiment using pressurized hot water to extract chemicals that were soluble in hot water from the cut pieces of fully blown never fill bottles. This provides a worst case scenario given the high pressure and temperature of the extracting aqueous phase. The second water-based screening experiment was a high volume stir-bar experiment method using full bottles from the actual storage experiment where the stir-bar was placed directly into the full water bottle, the bottle inverted, and the stir-bar extraction conducted on a Teflon lining placed into the bottle cap. This approach provided very low detection limits relative to the actual storage experiment measurements because of the higher volume. The approach also minimized potential for trace contamination because no transferred or additions were made to the water prior to extraction.

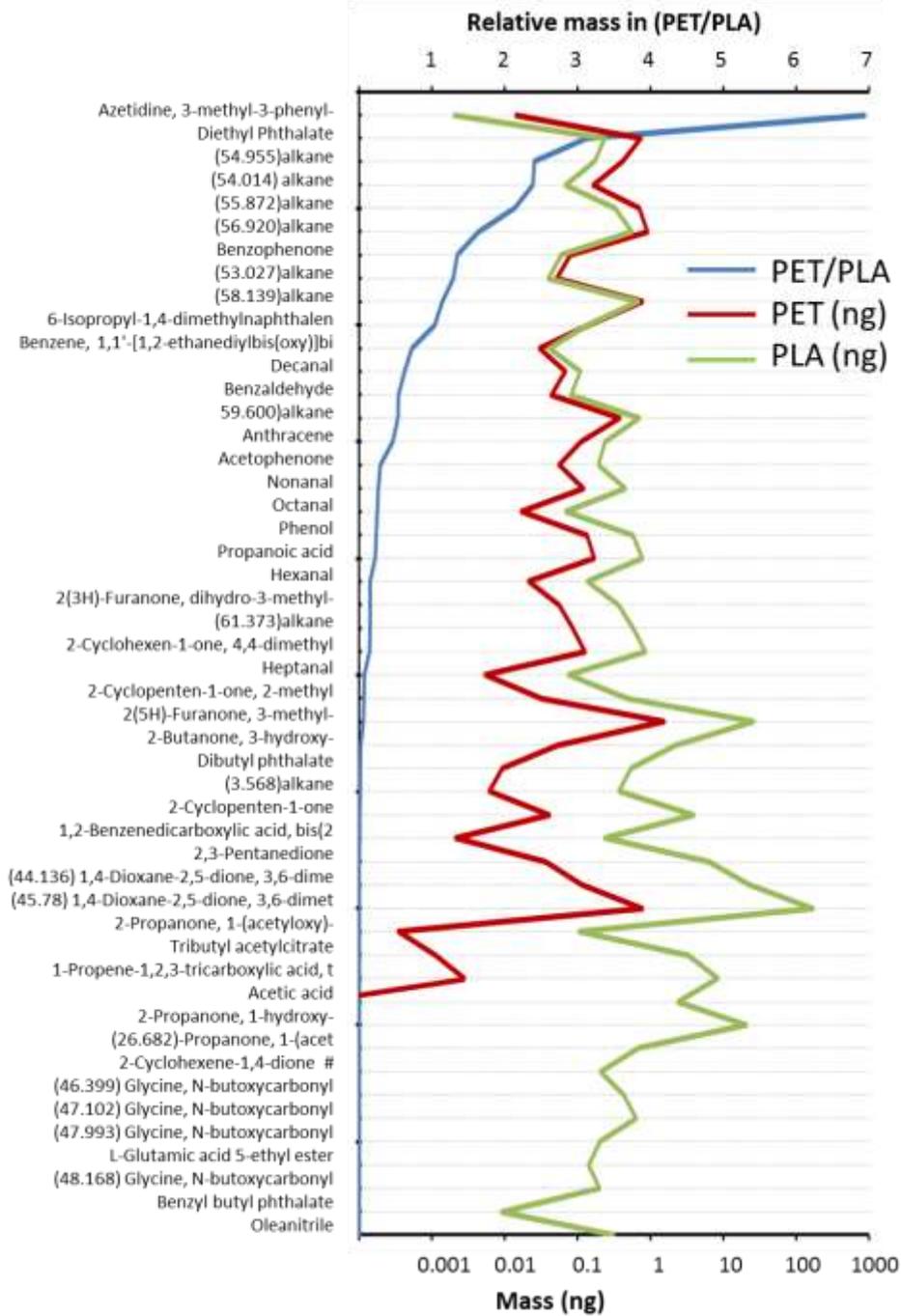


Figure 2. Comparison of direct thermal desorption results for PET and PLA. Ratio of the mass in PET relative to the mass in PLA is shown on top axis and the average mass in each plastic type is shown on bottom axis. The bottom axis is in log scale.

The chromatograms from the water-based screening experiments were scanned initially to identify target compounds present in the water. Then the chromatograms were referred to throughout the study to confirm or refute the presence of specific compounds detected during the storage experiments. The final list of target compounds detected in water contained in PET and PLA bottles during the storage experiment, and confirmed by the water-based screening experiments and the direct thermal extraction experiment, is provided in Table 2. The occurrence of each compound in the four PET manufactured bottles and the three PLA manufactured bottles are also listed in Table 2. The occurrence is based on the full bottle SBSE experiment. The alkanes detected by direct thermal desorption were not detected in the storage experiment or the water-based screening experiments, which illustrates the importance of solubility in potential leaching. Most alkanes have exceedingly low water solubility and, as such, will not migrate from a polymer surface into water. The higher volatility compounds with vapor pressures greater than ~ 0.1 mmHg were also not detected in the water samples from the storage experiment or the two screening experiments.

The fact that VOCs were detected during the direct thermal extraction screening experiment but not in the water samples may be in part related to the higher detection limit for VOCs (vapor pressure > 0.1 mmHg), or more specifically, for compounds with low capacity for sorption by the stir-bar (i.e., compounds with a low octanol/water partition coefficient less than ~ 3). Concentrations need to be in the high parts per billion to low parts per million ranges for compounds to be detected in water using the stir-bar extraction method.

Quantification of Chemical Migration during Storage Experiment

During the storage experiment, the PLA bottles from all three manufacturers that were stored at the high temperature condition (50 C°) failed sometime prior to the three-month sample collection point. The plastic matrix from the failed bottles was brittle and slightly cloudy or discolored. The bottles were initially filled with warm water to prevent pressurization of the bottles in the high temperature condition so, although pressure may have contributed to the PLA bottle failure, it is likely that the plastic matrix just became brittle and ruptured during storage at the highest temperature. It was also noted that for all PLA bottles in the longer storage periods, the PLA bottles noticeably lost water as indicated by a buckling or collapse of the bottle wall over time. Water loss from stored PLA bottles has been reported to be about one gram of water loss per week of storage (Du, 2012) under ambient conditions.

Both the room temperature storage and 35 C° storage measurements were successful for all bottles and all storage durations. The final dataset includes results for PET stored at room temperature overnight, 3 months, and 6 months and stored at 35 C° and 50 C° for three months and six months. The PLA results were inclusive for room temperature storage (22 C°) overnight, three months, and six months, and at 35 C° storage for three and six months.

Table 2. Final list of target compounds measured in PET and PLA storage experiments

#	Name	CAS #	Occurrence	
			PET	PLA
1	2-Ethyl-3-methoxy-2-cyclopentenone	25112-86-1	100%	100%
2	Benzothiazole	95-16-9	100%	100%
3	1,4-Dioxane-2,5-dione, 3,6-dimethyl-	95-96-5	50%	100%
4	1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-	4511-42-6	100%	100%
5	2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone	88725-82-0	100%	100%
6	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	719-22-2	75%	100%
7	4,6-di-tert-Butyl-m-cresol	497-39-2	50%	100%
8	Phenol, 2,4-bis(1,1-dimethylethyl)-	96-76-4	100%	100%
9	Diethyl Phthalate	84-66-2	100%	100%
10	1,1'-Biphenyl, 2,2',5,5'-tetramethyl-	3075-84-1	100%	100%
11	1,1'-Biphenyl, 3,3',4,4'-tetramethyl-	25570-02-9	25%	100%
12	Benzophenone	119-61-9	100%	100%
13	Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-	2219-84-3	100%	100%
14	Phenol, 4-(1,1-dimethylpropyl)-	80-46-6	100%	100%
15	4-Methyl-2-tert-octylphenol	4979-46-8	100%	100%
16	(52.583) unknown alkyl phenol	unknown01	100%	100%
17	(52.648) unknown alkyl phenol	unknown02	100%	100%
18	Phenol, 4-(1,1,3,3-tetramethylbutyl)-	140-66-9	100%	100%
19	3,5-di-tert-Butyl-4-hydroxybenzaldehy	1620-98-0	100%	100%
20	Phenanthrene	85-01-8	25%	100%
21	Diisobutyl phthalate	84-69-5	75%	100%
22	Ethanone, 2,2-dimethoxy-1,2-diphenyl	24650-42-8	100%	100%
23	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	6386-38-5	100%	100%
24	1-Methyldibenzothiophene	31317-07-4	25%	100%
25	Dibutyl phthalate	84-74-2	100%	100%
26	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca	82304-66-3	50%	100%
27	1-Propene-1,2,3-tricarboxylic acid, tributyl ester	7568-58-3	50%	67%
28	2,5-di-tert-Butyl-1,4-benzoquinone	2460-77-7	100%	100%
29	Tributyl acetylcitrate	77-90-7	50%	67%

Analysis of organic contaminants in stored water

The results SBSE-GCMS analysis for each bottle type and storage condition are presented in the tables in Appendix C. The average concentration (ppb) of each target compound at the six-month

storage point and 35 C° storage temperature was calculated for PET and PLA separately and the results are compared in **Error! Reference source not found.**. The compound specific concentrations range from < 10 ppt to ~ 1 ppb with some compounds more prominent in either PET or PLA as indicated by the point's deviation from the one-to-one line. Data points that are close to the one-to-one line indicate that the average concentrations are similar in both bottle types.

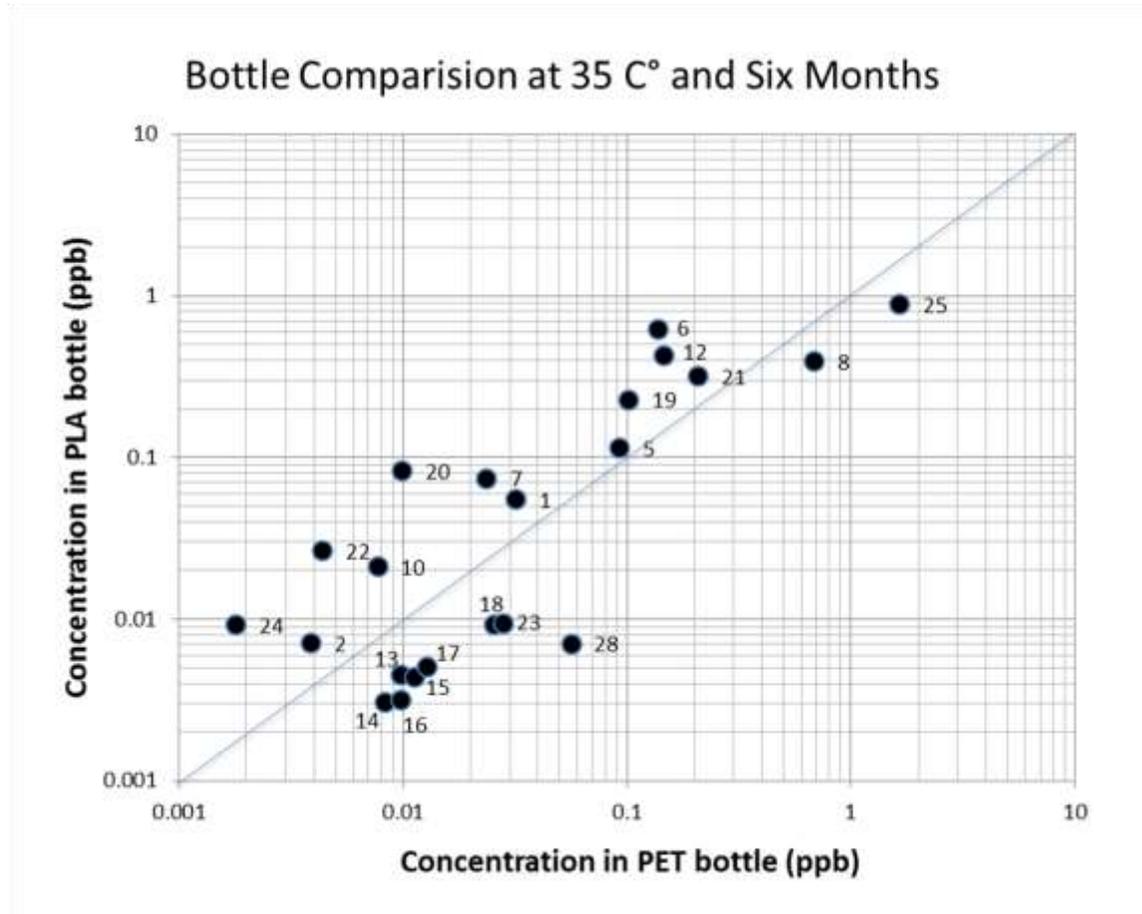


Figure 3. Comparison of the average concentration in the three PLA bottles stored 6 months at 35 C° and the average concentration in the four PET bottles stored under the same conditions. The numbers references the specific compounds in Table 2. The variability of the data for each compound and bottle type is illustrated in Figure 4. The diagonal line indicates the one-to-one relationship where compounds on this line are equal in both bottle types.

The majority of compounds in the final target list were measured at concentrations less than 0.1 ppb in the stored water, with only seven compounds rising above 0.1 ppb during the 35 C°, 6 month condition. For the PET, where we have data for bottles stored six months at 50 C°, only eight compounds had average concentrations above 0.1 ppb in the stored water. The variability of the data for each plastic bottle matrix across all manufacturers (n = 4 for PET, n = 3 for PLA) is illustrated in Figure 4 where the error bars represent ± 1 standard error of the mean (standard deviation / square root of the sample size). The data points without error bars indicate that results

did not include enough measurements above the limit of quantification to calculate a standard deviation.

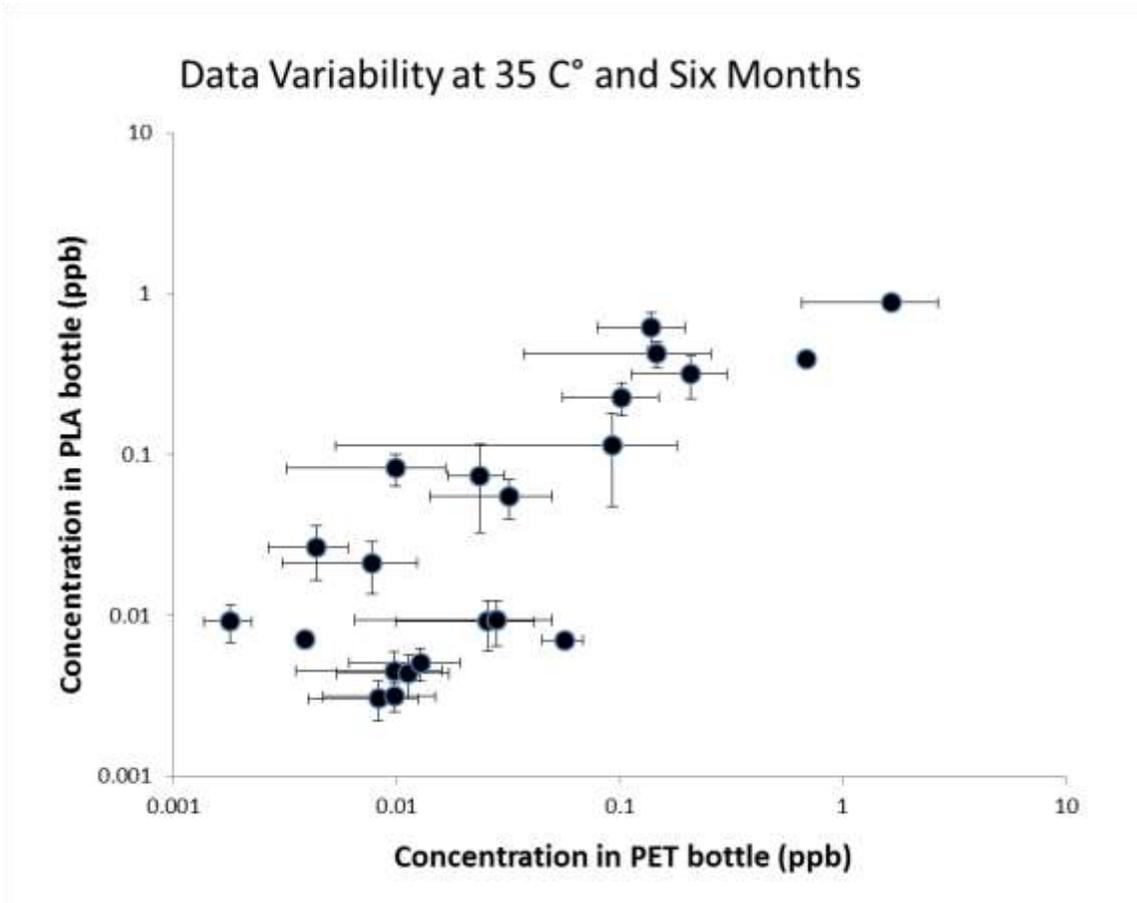


Figure 4. Copy of **Figure 3**. but with gridlines and labels removed to better show the error bars representing ± 1 standard error of the mean. In general, the variation for the PLA results was less than that for the PET results. Error bars were not calculated for samples that had only one measured value.

The concentration trends related to increasing storage temperature and increasing storage time were evaluated for the SBSE-GCMS data. To estimate the trend for increasing temperature, the ratio of concentrations measured at the higher temperature relative to the lower temperature for a specific storage duration was calculated for each bottle type/manufacturer combination (i.e., PET.A, PET.C... PLA.G). For example, the ratio of the measured concentration at 35 C° relative to that at 20 C° (room temperature) resulted in one data pair for three months and a second data pair for six months while the ratio at 50 C° relative to 35 C° resulted in two additional data pairs (three-months or six-months). This provides 15 possible data pairs for PET and six possible data pairs for PLA.

The average of the concentration ratios (higher temperature/lower temperature) was calculated for each plastic type and normalized to a 10 degree C° rise in temperature. This resulted in a concentration ratio representing the average relative increase in concentration (ppb) per 10 degree rise in storage temperature for all PET experiments and for all PLA experiments separately. A similar calculation was conducted to determine the average increase in concentration as a function of 3-month storage at a given temperature. The results are presented as a range (minimum – maximum) in Table 3 for the PET bottles and in Table 4 for the PLA bottles.

The percent occurrence (*N*) for each trend value in Tables 2 and 3 indicate the fraction of valid data pairs (i.e. the chemical was detected at both test conditions). For example, there are 15 possible data pairs for the temperature effect in PET and there are seven valid pairs for 2-Ethyl-3-methoxy-2-cyclopentenone (47 percent) that had both measured concentrations for both conditions above the limit of quantification.

The compounds not listed in Tables 3 and 4 (i.e., compounds 3, 4 and 26 from Table 2) did not have any detected concentration pairs to calculate trends relative to either temperature or storage time. Blank cells that report a value for *N* (e.g., diethyl phthalate in PET) indicate that there were valid measurements for that compound but the measurements did not show an increasing trend as a function of temperature and/or storage time. Results listed as a single value indicates that only one temperature and/or storage pair (i.e., measurements at two different temperatures or storage times) was detected so no range could be calculated.

Less than half of the compounds in Table 3 and Table 4 had consistently measured temperature and/or storage effects as indicated by the percentage of occurrence being less than 50 percent and the wide range of values for a given compound and plastic. The low number of occurrences and wide range are likely due to the exceedingly low concentrations that were measured in the water. However, it may also be that the effect is not linear across the range of temperatures (22 C° – 35 C°; 35 C° – 50 C°) and/or across the different storage durations (zero to three months and three to six months) but the measured concentrations were too low and the sample size too small to characterize the shape of the trend line across the different storage conditions.

Table 3. The relative increase in organic compounds (ppb) for PET per 10 degree rise in temperature or per 3-months of storage

Name	Temp. effect		Storage effect	
	min - max	N	min - max	N
2-Ethyl-3-methoxy-2-cyclopentenone	2.6 - 21.5	47%	1.6 - 1.8	50%
Benzothiazole	12.5	7%	3.4 - 3.8	17%
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone	1.9 - 9.3	80%	1.8 - 3.3	75%
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	1.8 - 11.5	80%	7.3 - 12.7	67%
4,6-di-tert-Butyl-m-cresol	1.0 - 1.4	60%	4.2	17%
Phenol, 2,4-bis(1,1-dimethylethyl)-	3.0	20%	2.1 - 4.0	25%
Diethyl Phthalate		7%		8%
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-	1.3 - 12.4	40%		25%
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-	1.6	13%		17%
Benzophenone	5.7 - 89.5	67%	1.6 - 2.4	67%
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-	1.4 - 3.0	93%	1.7 - 2.5	92%
Phenol, 4-(1,1-dimethylpropyl)-	1.5 - 3.3	87%	1.4 - 2.1	83%
4-Methyl-2-tert-octylphenol	1.6 - 3.5	87%	1.6 - 2.5	92%
(52.583) unknown alkyl phenol	2.5 - 3.4	67%	1.3 - 4.7	58%
(52.648) unknown alkyl phenol	1.4 - 2.7	93%	1.0 - 2.3	92%
Phenol, 4-(1,1,3,3-tetramethylbutyl)-	2.2 - 2.4	73%	1.9 - 2.3	75%
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	2.3 - 8.9	53%	2.4 - 17.2	50%
Phenanthrene	9.8 - 72.4	27%	3.4 - 5.2	33%
Diisobutyl phthalate	1.2 - 3.2	73%	2.7 - 3.9	75%
Ethanone, 2,2-dimethoxy-1,2-diphenyl-	7.7 - 162	73%	1.7 - 11.9	58%
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	1.3 - 2.5	80%	1.2 - 1.7	67%
1-Methyldibenzothiophene	2.4 - 5.8	53%	3.3 - 5.3	25%
Dibutyl phthalate		0%	14.9	8%
1-Propene-1,2,3-tricarboxylic acid, tributyl ester		0%		0%
2,5-di-tert-Butyl-1,4-benzoquinone	1.0 - 1.2	27%		0%
Tributyl acetylcitrate		0%	9.0	8%

Table 4. Relative increase in organic compounds (ppb) for PLA per 10 degree rise in temperature or per 3-months of storage

Name	Temp. effect		Storage effect	
	min - max	N	min - max	N
2-Ethyl-3-methoxy-2-cyclopentenone	2.6 - 7.0	83%	1.8 - 3.3	63%
Benzothiazole		0%		0%
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone	1.5 - 5.1	100%	2.2 - 3.3	75%
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	1.3 - 7.4	100%	7.5 - 15.8	88%
4,6-di-tert-Butyl-m-cresol	2.0	67%	9.8 - 24.8	38%
Phenol, 2,4-bis(1,1-dimethylethyl)-		0%	2.4 - 4.5	38%
Diethyl Phthalate	2.7	17%		0%
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-	1.1 - 1.3	83%	3.1	63%
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-		0%		0%
Benzophenone	10.4 - 103	100%	2.1 - 8.4	75%
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-	1.6 - 2.4	50%	1.1 - 2.5	50%
Phenol, 4-(1,1-dimethylpropyl)-	1.0 - 1.8	50%	1.1	38%
4-Methyl-2-tert-octylphenol	1.8	50%	1.1 - 3.6	50%
(52.583) unknown alkyl phenol	2.7	17%	1.4 - 3.1	38%
(52.648) unknown alkyl phenol	2.2 - 2.6	50%	1.1 - 2.5	50%
Phenol, 4-(1,1,3,3-tetramethylbutyl)-	1.9 - 2.1	83%	1.1 - 2.0	63%
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	3.4 - 11.8	100%	1.4 - 4.4	75%
Phenanthrene	2.3 - 15.7	100%	1.5 - 2.6	75%
Diisobutyl phthalate	1.0 - 1.6	100%	1.0 - 3.0	88%
Ethanone, 2,2-dimethoxy-1,2-diphenyl-	1.6 - 11.3	83%	1.6 - 6.0	75%
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	1.9 - 5.8	83%	1.3 - 2.3	63%
1-Methyldibenzothiophene	1.3 - 6.7	50%	3.4 - 5.6	38%
Dibutyl phthalate		17%		13%
1-Propene-1,2,3-tricarboxylic acid, tributyl ester		33%		50%
2,5-di-tert-Butyl-1,4-benzoquinone		0%		0%
Tributyl acetylcitrate		33%		0%

Analysis of elemental contaminants in stored water

The elemental analysis results from the ICP-MS measurements for the storage experiment are reported in Appendix D for all bottle type/manufacturer combinations. There were significantly elevated concentrations for many of the minerals commonly found in water including sodium, magnesium, silica, potassium, calcium and iron with lower levels in the sub ppb range for many of the trace elements. An analysis of the trend of concentration with increasing temperature and storage time was conducted as described for the organic compounds above. The results are given for both bottle types in Table 5.

Table 5. Relative increase in elements (ppb) per 10 degree rise in temperature or per 3-months of storage

Element	PET Bottles				PLA Bottles			
	Temperature		Storage		Temperature		Storage	
	min-max	N	min-max	N	min-max	N	min-max	N
Li		100%	1.0	80%		100%	1.0 - 1.1	75%
B		100%	1.9 - 2.7	100%		100%	1.1 - 8.5	100%
Na		100%	1.0 - 1.3	80%		100%	1.0 - 7.5	88%
Mg		100%	1.1	80%		100%	1.0 - 1.1	75%
Al		20%		33%		0%		0%
Si		73%	1.1	60%		100%	1.3 - 1.4	75%
K		100%	1.1 - 40.8	93%		100%	1.1 - 1.2	75%
Ca		87%	1.1 - 6.0	87%		100%	1.1 - 1.3	75%
Mn	1.5 - 1.8	93%	1.2 - 2.7	93%	9.2	100%	12.	100%
Fe		73%	1.3	67%	1.0 - 2.1	100%	1.1 - 3.1	100%
Se		93%	1.0 - 1.1	80%		100%	1.0 - 1.3	100%
Ni	2.9	73%	1.0 - 1.2	60%	2.5	83%	1.3 - 4.1	63%
Co		73%	1.0 - 1.5	67%		33%		25%
Cu		87%	1.4	87%	1.2	100%	1.7	100%
Zn		60%	11.0	53%		17%	1.4	50%
As	1.1 - 1.8	67%	1.1	53%		100%	1.4 - 1.6	75%
Rb		100%	1.0 - 1.1	100%		100%	1.0 - 1.2	100%
Sr		100%	1.5 - 6.4	100%		100%	1.1 - 1.6	88%
P	6.0	33%	2.8	33%		0%		0%
Mo		100%	1.1 - 2.1	87%		100%	1.0 - 1.1	75%
Sb	1.6 - 1.9	100%	1.1 - 1.7	100%		67%	1.2 - 1.2	63%
Ce		0%	1.4	7%		0%		0%
Pb	1.5	60%	1.3	40%	1.1	67%	1.8 - 2.8	63%
Sn		0%		0%	1.1 - 1.6	50%	2.8 - 2.8	25%

Several compounds were excluded from Table 5 either because the concentrations were below the quantification limit (i.e., $N = 0\%$) or the compound did not show an increasing trend in

concentration as a function of temperature or storage. These include Be, V, Cr, Ti, Ag, Cd, Cs, Ba, Eu, Bi, Th and U.

There were few elements in PET and PLA that showed an increasing trend with temperature. However, both types of plastic had a number of elements that exhibited an increasing trend with storage time as shown in Table 5. However, the relative change was typically small and those with larger changes were often dominated by a small number of measurements or represent a small absolute change in concentration.

Analysis of polar and high molecular weight compounds in stored water

Results from the LC-MS analysis are not included in this report. All samples were collected and analyzed and the data files were screened to identify major contaminants but the analyses were not formally quantified. The main compound identified in the initial screening of the chromatograms was polyethylene glycol (PEG), which was identified in both PET and PLA samples. PEG is a polyether compound that is used in a large number of consumer products and pharmaceutical and has a very low toxicity (Webster et.al, 2009). The LC-MS samples were not quantified because a significant amount of effort in this project was redirected to the screening experiments needed to identify and confirm unknowns in the SBSE-GCMS analysis. Resources were not available at the end of the project to finish quantifying the LC-MS samples. These data files have been archived and are available for future analysis as needed.

Uncertainty analysis for stored water measurements

In addition to characterizing variability across the bottles of a given plastic type as shown in PET to PLA comparison in Figure 4, several quality assurance (QA) measurements were conducted during the study. The QA measurements included blanks of the test water, replicate composite samples and triplicates from different bottles of the same type/manufacturer. Several blank samples were included for each of the analysis methods and the average of the resulting blank concentrations was subtracted from each sample prior to reporting results. Fourteen sets of duplicate measurements were conducted on the composite samples to quantify experimental error. In addition, two sets of triplicate measurements were included (PET.I and PLA.Fg) to quantify the variability of measured concentrations for bottles from the same lot and manufacturer.

The relative precision (standard deviation divided by the mean, reported as %CV) is the more useful metric for assessing performance and when low (< 25 percent for overall experimental precision) it always indicates good precision. However, when concentrations are very low, the relative precision values can be inflated. In these cases, the absolute precision is assessed because high relative precisions are only indicative of poor measurement precision if the absolute precision is also high. The relative precision (%CV), along with the absolute difference between replicate measurements (DIF, ppb) for each compound is reported under the column labeled "Duplicate" in Table 6. These values represent the overall experimental error associated with the SBSE-GCMS method. Most of the compounds had good precision (low %CV). Those compounds with a higher relative precision (e.g., 3,3',4,4'-tetramethylbiphenyl) had an average absolute difference between duplicate measurements that was below 50 ppt indicating good precision in the measurements at very low concentrations.

The variation in measurements for an individual bottle type/manufacturer was also characterized and is reported in Table 6 under the heading "Triplicate." These results measure the difference that can be expected across different bottles from the same type/manufacturer. Again, both the

relative precision (%CV) and absolute precision (DIF) are reported. Two compounds (Diisobutyl phthalate and Dibutyl phthalate) had somewhat higher relative precision (higher %CV) with absolute precision between 0.1 and 1 ppb. A 1 ppb difference between measurements from the different bottles of the same type/manufacturer is still a small number but the fact that the absolute precision is higher for the phthalates than for the other compounds may indicate that the phthalates are not intrinsic to the plastic but their detection in the water may be associated with other sources (caps, intermittent analytical background).

Table 6. Uncertainty in the SBSE-GCMS measurements

Compound	Duplicate		Triplicate	
	%CV	DIF	%CV	DIF
2-Ethyl-3-methoxy-2-cyclopentenone	14.7%	0.001	18.1%	0.010
Benzothiazole	27.7%	0.002	40.2%	0.006
1,4-Dioxane-2,5-dione, 3,6-dimethyl-				
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-			61.8%	0.006
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone	33.1%	0.010	18.5%	0.052
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	4.5%	0.002	22.7%	0.096
4,6-di-tert-Butyl-m-cresol	12.1%	0.001	48.0%	0.026
Phenol, 2,4-bis(1,1-dimethylethyl)-	19.6%	0.006	28.5%	0.098
Diethyl Phthalate	67.9%	0.025	32.0%	0.015
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-	24.8%	0.002	29.6%	0.009
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-	35.3%	0.041	30.9%	0.032
Benzophenone	5.9%	0.002	22.6%	0.090
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-	11.0%	0.001	23.6%	0.002
Phenol, 4-(1,1-dimethylpropyl)-	10.6%	0.000	23.4%	0.002
4-Methyl-2-tert-octylphenol	8.0%	0.000	17.6%	0.002
(52.583) unknown alkyl phenol	10.4%	0.001	18.9%	0.002
(52.648) unknown alkyl phenol	26.9%	0.001	17.3%	0.002
Phenol, 4-(1,1,3,3-tetramethylbutyl)-	9.0%	0.001	28.0%	0.005
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	14.8%	0.002	34.1%	0.065
Phenanthrene	8.3%	0.003	19.3%	0.021
Diisobutyl phthalate	13.3%	0.012	35.7%	0.103
Ethanone, 2,2-dimethoxy-1,2-diphenyl-	12.4%	0.001	14.9%	0.075
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	33.3%	0.005	27.2%	0.003
1-Methyldibenzothiophene	31.1%	0.001	24.8%	0.003
Dibutyl phthalate	17.3%	0.320	36.4%	1.042
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	71.8%	0.010		
1-Propene-1,2,3-tricarboxylic acid, tributyl ester			36.0%	0.019
2,5-di-tert-Butyl-1,4-benzoquinone			0.1%	
Tributyl acetylcitrate			44.2%	0.005

The uncertainty for the elemental analysis was also characterized and the results indicated good precision in the measurements with the average relative precision across all compounds of 5.3 percent (range 1.2 percent to 17 percent).

Chemical Prioritization for Screening Hazard Assessment

The chemicals described in the previous sections were prioritized for further scrutiny using the following factors:

1. Known or suspected toxicity
2. Detection in significant concentrations (> 1 ppb) during one or more of the conditions
3. Chemical relevance to plastic production.

Information about toxicity was reviewed and is documented in Appendix F with the key points of the review summarized below.

Prioritization based on detected concentrations was more relevant for organic compounds. In the elemental analysis, group 1 and 2 metals (e.g. sodium, calcium) and elements belonging to complex ions that commonly occur in water (e.g. phosphorus) were not considered for prioritization.

Based on the above prioritization factors, the substances listed in Table 7 were selected for inclusion in the exposure and hazard evaluation.

The prioritized organic compounds fall into three broad categories.

- *Phthalates*. Three phthalates were detected. These were prioritized because they are known to exhibit endocrine activity in mammals (See section on Health Hazard Data Review in the following section). Diisobutyl phthalate and dibutyl phthalate are both on the European Chemicals Agency's Candidate List of Substances of Very High Concern.
- *Alkylphenol derivatives*. We prioritized three compounds associated with antioxidants used in packaging materials (Löschner et al., 2011). 3,5-Di-tert-butylbenzoquinone and 3,5-di-tert-butyl-4-hydroxybenzaldehyde are oxidation products of the common preservative BHT (4-methyl-2,6-di-tert-butylphenol). However, BHT itself was not found in the analysis. These degradation products were prioritized because both could act as electrophiles which can form adducts with proteins leading to different toxic effects, and the quinone could act as an oxidant in biological systems. 2,4-Di-tert-butylphenol is a degradation product of a phosphite-based antioxidant. We detected it at significant concentrations; it has previously been found to leach into water from polypropylene kettles (Skjevraak et al., 2005).
- *Other aromatic compounds*. Benzophenone and phenanthrene are structurally similar to known endocrine disruptors and carcinogens. 2,2-Dimethoxy-1,2-diphenylethanone is normally used as a photoinitiator for radical reactions; as such, it could potentially exhibit radical reactivity in biological systems resulting in alteration of macromolecules and membranes.

We also prioritized four metals: Arsenic and lead are known to be highly toxic and should not be present in bottles. Antimony and tin are used in the production of PET and PLA, respectively

(Lithner et al., 2011, Mutsuga et al., 2007). Their detection here could be due to residual catalyst leaching from the bottles.

Table 7. List of Target Compounds for Exposure Assessment

Name	CAS#	Prioritization factors for selection
<i>Organic compounds (from GC-MS analysis)</i>		
Diethyl phthalate	84-66-2	Toxicity
Diisobutyl phthalate	84-69-5	Toxicity
Dibutyl phthalate	84-74-2	Concentration, toxicity
Benzophenone	119-61-9	Concentration, suspected toxicity
Phenanthrene	85-01-8	Suspected toxicity
2,2-Dimethoxy-1,2-diphenylethane	24650-42-8	Concentration, suspected toxicity
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	Relationship to other prioritized compounds, suspected toxicity
3,5-Di-tert-butylbenzoquinone	719-22-2	Concentration, suspected toxicity
2,4-Di-tert-butylphenol	96-76-4	Concentration
<i>Elements (from ICP-MS analysis)</i>		
Arsenic (As)	7440-38-2	Toxicity
Tin (Sn)	7440-31-5	Toxicity, use in PLA production
Antimony (Sb)	7440-36-0	Concentration, toxicity, use in PET production
Lead (Pb)	7439-92-1	Toxicity

Discussion

Review of Concentration and Trends for Prioritized compounds

We examined the analysis data for the prioritized compounds listed in Table 7. The maximum concentration over all measurements is listed along with the averages of concentrations for each of the prioritized chemicals in Table 8. The average concentration is used to represent the exposure concentration in water stored in the different bottle types. We looked for trends in concentration in accordance with storage time and temperature that would indicate leaching from the plastic (Tables 3, 4 and 5). The trends were also evaluated graphically to further explore

trends in concentration related to temperature and storage time and the figures are provided in Appendix E.

For most of the prioritized compounds, we found clear trends of increased concentrations with higher temperatures and longer storage times, in both PET and PLA bottles. For example, antimony (Sb) showed a clear trend with temperature and storage time in never-filled PET bottles. Commercially-filled bottles (PET-I) showed the same trend but at much lower levels. On the other hand, antimony was barely detected in PLA, with no trend. Tin (Sn) was only detected in PLA bottles (specifically PLA-F; only trace in PLA-G). There was no clear trend, but Sn was detected only at three and six months. The patterns in the detection of these two metals are consistent with their catalytic use in the polymerization of PET (Sb) and PLA (Sn).

Diethyl phthalate, dibutyl phthalate, arsenic (As), and lead (Pb) showed no apparent trend with storage time and temperature, and they were not detected in most samples. The phthalates were discussed earlier and given their intermittent detection and lack of trend with temperature or storage time, these organic compounds were likely not associated with the plastic matrix of the bottles. Lead was detected primarily in the initial samples taken after 12 hours storage, and was not detected in commercially filled bottles. Like the phthalates, arsenic and lead were either not detected consistently in the water and/or lacked a clear trend with temperature and storage time. We concluded that these four substances are not leaching from the plastic, and therefore we did not assess potential exposures to these substances from bottles.

Exposure assessment

The prioritized chemicals were detected at a range of concentrations in each plastic depending on storage time and temperature. In order to model human exposure from drinking bottled water, we selected a reasonable storage condition from among the experimental conditions used in the study. For each chemical and each plastic type (i.e., PET or PLA), we calculated the exposure concentration (see Table 8) as the average concentration detected after three months of storage at 35 °C. These concentrations were typically much lower than those observed after six months of storage, or after storage at 50 °C. Some chemicals were detected in too few samples after such storage to calculate the average exposure concentration: phenanthrene and 2,4-di-tert-butylphenol in PET bottles, and tin in both PET and PLA bottles. We conclude that these chemicals do not appreciably leach from the bottles, except under extreme conditions. Typical storage conditions used by consumers and stores would typically not be at the highest temperature and longest storage period used in this study.

Table 8 Maximum and exposure concentrations for prioritized chemicals.

Name	CAS#	Maximum concentration	
		$\mu\text{g/L}^{\text{a}}$	Sample
Diisobutyl phthalate	84-69-5	0.482 ± 0.064	PLA-Fc T2S2
Benzophenone	119-61-9	1.280 ± 0.076	PET-A T3S2
Phenanthrene	85-01-8	0.318 ± 0.026	PET-A T3S2
2,2-Dimethoxy-1,2-diphenylethanone	24650-42-8	2.080 ± 0.258	PET-A T3S2
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	0.882 ± 0.130	PET-C T3S2
3,5-Di-tert-butylbenzoquinone	719-22-2	1.650 ± 0.074	PET-C T3S2
2,4-Di-tert-butylphenol	96-76-4	1.460 ± 0.286	PET-A T3S2
Tin (Sn)	7440-31-5	0.074 ± 0.008	PLA-Fg T1S1
Antimony (Sb)	7440-36-0	5.930 ± 0.44	PET-C T3S2
			Exposure concentration ($\mu\text{g/L}^{\text{b}}$)
	Average ($\mu\text{g/L}^{\text{b}}$)	PET	PLA
Diisobutyl phthalate	0.482 ± 0.064	0.144 ± 0.186	0.290 ± 0.153
Benzophenone	1.280 ± 0.076	0.051 ± 0.076	0.272 ± 0.046
Phenanthrene	0.318 ± 0.026	^c	0.032 ± 0.002
2,2-Dimethoxy-1,2-diphenylethanone	2.080 ± 0.258	0.001 ± 0.001	0.006 ± 0.001
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	0.882 ± 0.130	0.054 ± 0.054	0.073 ± 0.015
3,5-Di-tert-butylbenzoquinone	1.650 ± 0.074	0.015 ± 0.012	0.112 ± 0.133
2,4-Di-tert-butylphenol	1.460 ± 0.286	^c	0.117 ± 0.019
Tin (Sn)	0.074 ± 0.008	^c	^c
Antimony (Sb)	5.930 ± 0.44	0.632 ± 0.619	0.007 ± 0.001

^a Reported with experimental uncertainty.

^b Reported with standard deviation of the average.

^c Detection too low to calculate the average for 3 months storage at 35 °C.

Using the exposure concentrations described above, and assuming all water consumed was from a bottled source, we calculated daily intake (mg/kg) for two age ranges, using mean and 95th percentile water intake rates according to the U.S. EPA (2011).

$$\text{Daily intake } (\mu\text{g kg}^{-1}\text{d}^{-1}) = \text{concentration } (\mu\text{g/L}) * \text{intake rate per day } (\text{L kg}^{-1}\text{d}^{-1})$$

Mean daily drinking water intake

Children age 2-3: 0.026 L kg⁻¹d⁻¹

Adults age 21-65: 0.016 L kg⁻¹d⁻¹

95th Percentile daily drinking water intake

Children age 2-3: 0.062 L kg⁻¹d⁻¹

Adults age 21-65: 0.042 L kg⁻¹d⁻¹

The results of the preliminary exposure assessment are shown in Table 9 for PET water bottles and in Table 10 for PLA water bottles.

Table 9 Estimated human exposures to chemicals from PET bottled water ($\mu\text{g kg}^{-1}\text{d}^{-1}$).

Substance	Children, age 2-3	
	mean	95 th %ile
Diisobutyl phthalate	0.0037 \pm 0.0048	0.0089 \pm 0.0115
Benzophenone	0.0013 \pm 0.0020	0.0031 \pm 0.0047
Phenanthrene	1	1
2,2-Dimethoxy-1,2-diphenylethanone	0.000038 \pm 0.000018	0.000091 \pm 0.000044
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	0.0014 \pm 0.0014	0.0034 \pm 0.0033
3,5-Di-tert-butylbenzoquinone	0.00040 \pm 0.00032	0.0010 \pm 0.0008
2,4-Di-tert-butylphenol	1	1
Antimony (Sb)	0.016 \pm 0.016	0.039 \pm 0.038
Substance	Adults, age 21-65	
	mean	95 th %ile
Diisobutyl phthalate	0.0023 \pm 0.0030	0.0060 \pm 0.0078
Benzophenone	0.0008 \pm 0.0012	0.0021 \pm 0.0032
Phenanthrene		
2,2-Dimethoxy-1,2-diphenylethanone	0.000023 \pm 0.000011	0.000061 \pm 0.000030
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	0.00087 \pm 0.00086	0.0023 \pm 0.0023
3,5-Di-tert-butylbenzoquinone	0.00025 \pm 0.00020	0.00064 \pm 0.00052
2,4-Di-tert-butylphenol		
Antimony (Sb)	0.010 \pm 0.010	0.027 \pm 0.026

¹ Compounds not detected in PET bottles.

Table 10 Estimated human exposures to chemicals from PLA bottled water ($\mu\text{g kg}^{-1}\text{d}^{-1}$).

Substance	Children, age 2-3	
	mean	95 th %ile
Diisobutyl phthalate	0.0075 ± 0.0040	0.018 ± 0.009
Benzophenone	0.0071 ± 0.0012	0.017 ± 0.003
Phenanthrene	0.00083 ± 0.00006	0.0020 ± 0.0001
2,2-Dimethoxy-1,2-diphenylethanone	0.00015 ± 0.00001	0.00036 ± 0.00003
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	0.0019 ± 0.0004	0.0045 ± 0.0009
3,5-Di-tert-butylbenzoquinone	0.0029 ± 0.0035	0.0070 ± 0.0083
2,4-Di-tert-butylphenol	0.0030 ± 0.0005	0.0072 ± 0.0012
Antimony (Sb)	0.00017 ± 0.00003	0.00041 ± 0.00008
Substance	Adults, age 21-65	
	mean	95 th %ile
Diisobutyl phthalate	0.0046 ± 0.0024	0.012 ± 0.006
Benzophenone	0.0043 ± 0.0007	0.011 ± 0.002
Phenanthrene	0.00051 ± 0.00004	0.0013 ± 0.0001
2,2-Dimethoxy-1,2-diphenylethanone	0.000093 ± 0.000008	0.00024 ± 0.00002
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	0.0012 ± 0.0002	0.0031 ± 0.0006
3,5-Di-tert-butylbenzoquinone	0.0018 ± 0.0021	0.0047 ± 0.0056
2,4-Di-tert-butylphenol	0.0019 ± 0.0003	0.0049 ± 0.0008
Antimony (Sb)	0.00011 ± 0.00002	0.00028 ± 0.00005

Conclusion

Chemical Migration Study and Preliminary Hazard Assessment

Forty-nine organic compounds were identified in PET and PLA by direct thermal desorption. Twenty-nine organic compounds were subsequently identified and quantified in stored water contained in PET or PLA. In addition, 24 elements were identified to consistently be found in stored water in PET and/or PLA. Many of the compounds identified in the stored water showed increasing trends in concentration with increasing storage time and storage temperature. Screening all compounds and storage conditions, and considering several prioritization criteria, the list of target compounds was reduced to include nine organic compounds and four elements (Table 7). This list was further reduced to include a total of eight substances based on evidence in the trend analysis that indicated that several of the compounds were not likely associated with the plastic bottles.

The final eight prioritized chemical substances were detected in bottled water that, based on their concentrations over a range of storage conditions, appear to be leaching into water from the PET or PLA-based material of the container under plausible storage conditions. These include diisobutyl phthalate (DIBP), benzophenone, phenanthrene (PLA only), three alkylphenol derivatives suspected to be the degradation products of antioxidants used in packaging materials, and the metal antimony. We summarized the hazard information for these substances and estimated the exposure levels to children and adults, using a range of exposure scenarios established by U.S. EPA (EPA 2011).

Several of these substances are known to be hazardous, including: benzophenone, a known carcinogen; and DIBP, a known endocrine disruptor affecting male reproductive development at low doses.

Although there are no exposure limits in water (MCL) established for these substances, our preliminary analysis indicates that, under the conditions of this experiment, exposure would occur in concentrations too low to pose significant health risk, based on the toxicity information publicly available for these substances.

For example, under the conditions of these experimental observations, a pregnant woman exposed at the 95th percentile level would be exposed to 0.006 $\mu\text{g kg}^{-1}\text{d}^{-1}$ DIBP from PET bottled water, or 0.012 $\mu\text{g kg}^{-1}\text{d}^{-1}$ DIBP from PLA bottled water. Changes in fetal testicular testosterone production caused by DIBP are thought to be the most sensitive endpoint for DIBP effects on male reproductive development, with a NOAEL of 100 $\text{mg kg}^{-1}\text{d}^{-1}$, which is eight orders of magnitude higher than our estimated exposure level based on the experimental storage conditions described in this report.

Study Limitation

The findings of this experiment do not suggest an immediate health risk posed by chemicals leaching from PET or PLA water bottles. However, it is important to remain cognizant of the many gaps in toxicity data, and the reality that people are exposed to many of these substances from multiple sources whose impacts can be cumulative. Therefore, even low level exposures, when known, can provide an opportunity to incrementally reduce exposures in the population.

Although the study was designed to identify and quantify a wide range of chemical classes using multiple sampling and analysis methods, and the results produced concentration data with good precision (Table 6), many of the compounds measured were at the lower range of the method detection limits. The low concentrations made the chemical analysis challenging, particularly for the organic compounds analyzed for with full scan mass spectrometry. Background contamination in the water used in the experiments and trace contamination introduced during sample processing sometimes masked the low level target concentrations.

Because an unanticipated amount of effort and additional experimentation including direct thermal desorption and two additional water-based screening analyses was needed to provide a comprehensive list of target chemicals in PET and PLA, we were unable to complete the quantification of data from the LCMS analysis. This could result in missing the possible presence of compounds with very low volatility but that are highly polar compounds such as acids and bases in the stored water. However, the screening review of the LCMS data did not show elevated unknown peaks except for the presence of polyethylene glycol oligomers which are not considered to be toxic.

Chemical identification in this study was based on carefully matching mass spectra to published libraries using both the raw mass spectral fingerprints and deconvoluted mass spectra. This provides high quality matches but final confirmation of chemical identity should also include analysis of pure standards under the same study conditions. Many of the compounds identified in this study do not have readily available pure standards so the final verification step for verification of compound identity was not completed.

The study used warm carbon filtered tap water as the fill water during the storage experiments starting with fully-blown, never-filled bottles provided by manufacturers. We did not consider other processes related to the bottle filling such as labeling, ozonation of fill water, and pre-fill bottle washing. Nor did the current study consider difference in fill water used by different manufacturers. The difference between the commercially filled bottle included in this study and the never-filled bottles indicates that there are potential sources and/or removal processes for contaminants in the commercial bottling process that are were not included in this study.

Finally, it is likely that the chemical make-up of plastic used in water bottles differs across manufacturers and may change over time, particularly for PLA where issues with water loss and storage stability will require changes in chemistry and/or production methods. It is unclear how these changes will influence migration of chemicals into stored water and this study does not address these possible changes to PET/PLA chemistry.

Future Work

There are several opportunities to build on the work described in this report. These include:

- Improve upon the full bottle analysis method using SBSE to provide a more efficient and economical screening tool for testing off-the-shelf commercially filled bottles.
- Completion of LCMS analysis to confirm that the levels of oligomers and polar contaminants do not pose a health hazard.
- Verify the identity of target compounds using pure standards where available.

- Provide a more detailed analysis of the temperature effect for PLA leading up to failure of the bottles at 50 C° with increased resolution in both time and temperature.
- Test the effect of specific bottling processes such as ozonation of fill water, bottle washing before filling and labeling.
- Test the effect of storage conditions related to environmental exposures such as extended storage in direct sunlight or storage in areas with potentially elevated chemical concentrations, i.e., hot vehicle trunk space.
- Characterize the influence of different fill liquid parameters (pH, hardness, ...) on the migration of compounds from containers.

The most important future work based on our experience from this project would be to further develop the full-bottle stir-bar sorptive GCMS method to provide a cost effective way to screen large numbers of commercially filled and laboratory filled bottles under a range of storage conditions. The method was demonstrated during this project to be a much simpler method providing improved sensitivity and less potential for introduction of trace contaminants into the sample. A field ready method could be available by adding a custom fit glass cap liner for the stir bar to rest on during extraction and by preparing a standard addition calibration with internal standard to be added to the fill water with a small aliquot (~ 5 ml) of methanol then optimize stirring time.

A simplified, cost effective sampling and analysis method, such as the full bottle SBSE-GCMS method, could facilitate the development of a database of compounds that are actually measured in fill water stored in commercially filled PET or PLA bottles. Such a database would be much more useful than the comprehensive lists of potential contaminants (Appendix A and B) although such comprehensive lists provide useful initial screening data for unknown contaminants in water and along with information about potential sources. A database of actual measured contaminants in a statistically relevant sample of fill water stored in PET and PLA could provide valuable information about trends in water quality over time and baseline data for comparison of new measurements. A database of actual target compounds in fill water stored in the different plastic matrixes will have the added benefit of leading to improvements in the analytical methods including the use of select ion monitoring to reduce detection and quantification limit over full scan methods.

This study demonstrated the importance of storage time and temperature but there are several other factors that could influence the migration of compounds from plastic bottle matrixes into stored water. These factors include parameters related to the preparation and filling of bottles such as ozonation and bottle washing. The factors also include parameters related to the storage environment such as direct sunlight and chemically contaminated storage areas (i.e., vehicle trunk space or garage with elevated fuel related hydrocarbons). These factors should be systematically evaluated for influence on compound migration into fill water.

Toxicological data on the specific compounds found in bottled water is limited. There are a number of compounds measured in bottled water that do not have sufficient toxicological data to support a hazard or risk assessment. Methods based on qualitative structural activity relationships are available (Lapenna et.al, 2010) and may be useful for screening and prioritizing compounds that lack relevant toxicity data. The performance of existing QSAR models and their relevance to water bottles studies should be evaluated.

Abbreviations and Acronyms

%CV – relative difference in terms of percent coefficient of variation

AMDIS – automated mass spectral deconvolution and identification system

ASE – accelerated solvent extraction

BHT – butylated hydroxyl toluene

CalRecycle – Department of Resources Recycling and Recovery

CAS# – Chemical abstract number

CRM – Carcinogenic, reproductive, mutagenic toxicity

DIBP – diisobutyl phthalate

DIF – absolute difference between two replicate samples

DNA – Deoxyribonucleic acid

DOE – U.S. Department of Energy

DTSC – California Department of Toxic Substances Control

FaST – Faculty and Student Teaching Internship

GC/MS – gas chromatography mass spectroscopy

GRAS – Generally recognized as safe

HPLC – high pressure (or high performance) liquid chromatography

IARC – International Agency for Research on Cancer

ICP-MS – inductively coupled plasma mass spectrometry

LBNL – Lawrence Berkeley National Laboratory

LC-MS – Liquid chromatography mass spectroscopy

LD₅₀ – Median lethal dose in animal studies

LLE – liquid liquid extraction

LV-VOC – low volatility volatile organic compound

MCL – maximum contaminant level

MeOH – methanol

NIH – National Institutes of Health

NIST – National Institute of Science and Technology

NSF – National Science Foundation

PEG – polyethylene glycol
PET – Polyethylene terephthalate
PHA – Polyhydroxyalkanoate
PLA – Polylactide
ppb – parts per billion
ppt – parts per trillion
QA – quality assurance
QSAR – qualitative structural activity relationship
S.E. – Standard Error of the Mean
SBSE – stir-bar sorptive extraction
SPME – solid phase micro extraction
SVOC – semi-volatile organic compound
TD-GC/MS – thermal desorption gas chromatography mass spectroscopy
UCB – University of California, Berkeley
USEPA – U.S. Environmental Protection Agency
VOC – volatile organic compound

Appendix A: Literature Review: Leaching of Migrants into Beverages Bottled in PET Beverage Container

Introduction

Polyethylene terephthalate (PET) is a widely used polymer for bottling water, mineral water, and carbonated beverages worldwide. Approximately 8.6 billion beverages bottled in PET were sold in California during 2008 (California Department of Conservation 2009). PET is considered a good packaging material for beverages due to its strength and permeability properties (Ozlem 2008).

There is some concern regarding the leaching of compounds from PET into beverages in PET bottles. It is well known that food may become contaminated with the components of some plastics by a diffusion process known as migration (Morelli et al. 1997). Begley and Hollifield (1989) stated that leached compounds from PET packages typically consist of initial reactants, including monomers, and reaction by-products such as low molecular weight oligomers.

This paper summarizes several pertinent scientific studies which have investigated compounds that leach into beverages from PET bottles. This paper does not include information about other types of PET packaging or regarding beverages packaged in recycled PET (rPET).

In the studies summarized in this paper, compounds that leached into beverages from PET included: acetaldehyde, formaldehyde, propanal, nonanal, glyoxal, propionaldehyde, n-butylaldehyde, antimony, acetone, oligomers (including the first series cyclic trimer, the first series cyclic tetramer, the first series cyclic dimer, the second series cyclic trimer), terephthalic acid, isophthalic acid, and ethylene glycol.

The majority of compounds detected in beverages bottled in PET were below worldwide recommended threshold limits, with a couple of exceptions. One acetaldehyde migration study detected two brands of water that contained acetaldehyde concentrations above the Japan threshold limit of 2 µg/L. A migration study by Westerhoff et al. showed levels of antimony in bottled water above the U.S. EPA's threshold of 6 µg/L after increased storage time and increased temperature.

Overview of Acetaldehyde and Formaldehyde Studies

During high temperature processing of PET, such as injection molding, degradation reactions generate by-products (Choodum et al. 2007). Acetaldehyde forms during the production of PET as a product of thermal degradation (Ozlem 2008). The high temperature used in the final state of the bottle preform production from PET causes thermal degradation of the polymer and contributes to forming a high concentration of acetaldehyde in the polymer structure (Dabrowska et al. 2003). Although acetaldehyde is a volatile compound, some of it remains in the bottle and can leach into beverages placed into these bottles due to acetaldehyde's high water solubility (Ozlem 2008). Wyatt (1983) found that the level of acetaldehyde produced during PET beverage bottle manufacturing can be reduced by controlling processing conditions, especially the heat history of the polymer.

Acetaldehyde is a chemical of concern because it has been classified as a probable human carcinogen (U.S. EPA 1987) and as a possible human carcinogen (International Agency for Research Center on Cancer 1985). The National Toxicology Program (NTP) in the Eleventh Annual Report on Carcinogens classified acetaldehyde as “reasonably anticipated to be a human carcinogen” based on sufficient evidence of carcinogenicity in experimental animals (NTP 2005).

Regulatory agencies set limits on migration of chemicals into food and beverages from packaging. For example, European Commission Directive 2002/72/EC stipulates the migration limit for acetaldehyde is 6 mg/kg (6 ppm) per bottle (2002/72/EC).

Formaldehyde is also a chemical of concern. Some studies have suggested that long-term occupational exposure to formaldehyde is linked to certain types of cancer such as leukemia (National Cancer Institute 2009) and it has been classified as a human carcinogen (IARC 2006). Exposure to formaldehyde in the air at levels exceeding 0.1 ppm may cause some individuals to experience adverse effects such as watery eyes, burning sensations in the eyes, nose, and throat, coughing, wheezing, nausea, and skin irritation. Some people are very sensitive to formaldehyde, whereas others have no reaction to the same level of exposure (National Cancer Institute 2009).

Several researchers have studied the migration of acetaldehyde in beverages packaged in PET, but there are only a few studies on formaldehyde migrating into bottled water. One study showed that PET products contain formaldehyde to the same extent as acetaldehyde (Mutsuga et al. 2005).

Acetaldehyde and Formaldehyde Study Summaries

Ozlem, KE. Acetaldehyde migration from polyethylene terephthalate bottles into carbonated beverages in Türkiye. *International Journal of Food Science and Technology*. (2008) 43: 333-338.

Ozlem studied the acetaldehyde migration potential of PET bottles used for carbonated beverages and also determined the effect of storage and temperature on acetaldehyde migration. Carbonated beverage samples were obtained from four different companies after the beverages were bottled. The samples were stored at 5, 20, and 40 °C for six months. Analyses of the samples were carried out at 0 day, then at 2, 4, and 6 months using a gas chromatograph coupled with a flame ionization detector (GC/FID).

Concentrations of acetaldehyde in the four different beverages ranged from 18.5 ppb to 359 ppb at Day 0. Both temperature and storage length were determined to have an effect on the increased concentration of acetaldehyde. Concentrations of acetaldehyde of beverages stored for 6 months at 40 °C ranged from 1.63 ppm to 130 ppm, which is above the European Commission acceptable threshold of 6 ppm for acetaldehyde. This study did not state the type of sampled carbonated beverages, although the study implies the beverages were soft drinks.

Choodum A, Thavarungkul P, Kanatharana P. Acetaldehyde residue in polyethylene terephthalate (PET) bottles. *Journal of Environmental Science and Health Part B*. (2007) 42: 577-583.

Choodum et al. developed a simple sample preparation technique to determine rapid analysis of acetaldehyde residue in PET. This study measured acetaldehyde residue ranging from 0.4 to 1.1 ng/mL in freshly blown PET bottles. It is noteworthy that this study measured acetaldehyde directly from the bottle and not from the beverage within.

Nijssen B, Kamperman T, Jetten J. Acetaldehyde in mineral water stored in polyethylene terephthalate (PET) bottles: Odour threshold and quantification. Packaging Technology and Science. (1996) 9: 175-185.

Nijssen et al. analyzed mineral water stored in PET bottles. This study found no acetaldehyde in still water above the detection level of 0.5 ug/L, but the concentration of acetaldehyde in carbonated mineral water increased steadily with increased storage time. The study found acetaldehyde concentrations up to 100 µg/L in carbonated water. The bottles were stored at room temperature and the water was analyzed at 2, 6, and 12 weeks of storage. The analysis was performed using headspace gas chromatography with a flame ionization detector and had a limit of detection of 0.5 ug/L.

Dabrowska A, Borcz A, Nawrocki J. Aldehyde contamination of mineral water stored in PET bottles. Food Additives and Contaminants. (2003) 20(12): 1170-1177.

Dabrowska et al. analyzed carbonated mineral water bottled in PET in Poland. The study detected analytes of interest in the samples including acetaldehyde, formaldehyde, propanal, nonanal, and glyoxal. The study found that acetaldehyde concentrations in the water were dependent on the amount of acetaldehyde in the PET bottle. The temperature, storage time, and CO₂ concentration were found to contribute to the migration of aldehydes from PET bottle walls to mineral water. The higher pressure of the carbonated waters, and not CO₂ itself, appears to be responsible for the higher concentrations of acetaldehyde.

This study used carbonated natural mineral water stored in glass bottles and in PET bottles. The aldehyde compounds were monitored for 170 days using a gas chromatograph coupled with an electron capture detector (GC/ECD). A significant difference was observed between the amounts of formaldehyde and acetaldehyde in the water stored in glass versus the water stored in PET bottles. The water in the PET bottles had a significantly higher concentration of formaldehyde and acetaldehyde than the water stored in the glass bottles. On the 170th storage day, the measured concentration of formaldehyde was 60.0 ug/L and acetaldehyde was 78 ug/L in the water bottled in PET.

This study also compared carbonated to non-carbonated water bottled in PET. The concentration of total aldehydes identified after six storage days was three times higher in carbonated water versus non-carbonated water. The acetaldehyde concentration was five times higher in the carbonated versus non-carbonated water. It is likely that the pressure of CO₂ on the bottle walls facilitates migration of carbonyls into the water.

This study also examined the influence of acetaldehyde content in PET material using two different sets of bottles: bottles made from preforms fabricated within the first minutes after starting the machinery (these bottles tend to have higher concentrations of acetaldehyde), and bottles made from preforms fabricated after 60 minutes of production (these bottles tend to have lower concentrations of acetaldehyde). The bottles were filled with carbonated mineral water and stored in a dark place at room temperature for 4, 10, and 16 weeks. At 4, 10, and 16 weeks, acetaldehyde concentrations were determined of the water stored in both bottle sample types and in the bottle walls themselves. Acetaldehyde concentration in the water increased with storage time. The higher the level of acetaldehyde in the bottle walls, the higher the acetaldehyde concentration found in the water.

The study also examined the migration of carbonyl compounds from polypropylene bottle caps. Eight caps were cut into small pieces and extracted with deionized water for 2, 5, and 15 hours at 20 °C and 60 °C. Formaldehyde, acetaldehyde, and acetone concentrations were detected. Concentrations of each compound increased with increasing temperature and increased time of extraction.

Mutsuga M, Kawamura Y, Sugita-Konishi Y, Hara-Kudo Y, Takatori K, Tanamoto K. Migration of formaldehyde and acetaldehyde into mineral water in polyethylene terephthalate (PET) bottles. Food Additives and Contaminants. (2006) 23(2): 212-218.

Mutsuga et al. conducted a study to measure formaldehyde and acetaldehyde migration into mineral water from PET bottles. Twenty PET-bottled mineral water samples were purchased in Japan; six were bottled in Japan, 11 were bottled in Europe, and three were bottled in North America. The water sampled from Japanese brand bottled water contained concentrations of formaldehyde in the range of 10.1 to 27.9 ug/L and acetaldehyde in the range of 11.3 to 107.8 ug/L. Three of the 11 European brands sampled, contained formaldehyde at concentrations of 7.4 to 13.7 ug/L and acetaldehyde at levels of 35.9 to 469 ug/L. Two of the three North American bottled waters sampled contained levels of formaldehyde at 13.6 to 19.5 ug/L and acetaldehyde at 41.4 to 44.8 ug/L.

Nawrocki J, Dabrowska A, Borcz A. Investigation of carbonyl compounds in bottled waters from Poland. Water Research. (2002) 36: 4893-4901.

Samples of mineral water were purchased on the retail market (13 non-carbonated and 14 carbonated), in three different size bottles, from 14 different manufacturers, and were analyzed in this study. Formaldehyde, acetaldehyde and acetone were the most important carbonyls identified. This study determined concentrations of formaldehyde (2.2 to 96.1 ug/L), acetaldehyde (0.9 to 317.8 ug/L), and acetone (5.1 to 125.6 ug/L) in bottled water. Further, increased storage time and temperature showed an increase in concentrations in the water samples. This study showed that the content of aldehydes gradually increased over a period of eight to nine months and then began to decrease. Samples were stored in the dark at 4 °C and in the sunlight at 30 °C. High concentrations of acetaldehyde (more than 100 ppb) were found in carbonated bottled water. The authors concluded that the carbonation of water, sunlight, and high temperature enhance the process of migration or aldehydes formation from PET bottles into water.

Sugaya N, Nakagawa T, Sakurai K, Morita M, Onodera S. Analysis of aldehydes in water by headspace-GC/MS. Journal of Health Science. (2001) 47(1): 21-27.

This study focused on developing a sensitive and selective method for the quantification of formaldehyde, acetaldehyde, propionaldehyde, and n-butyraldehyde in bottled water samples. The study determined aldehyde concentrations in commercial mineral water bottled in PET. Formaldehyde was detected in the range of not detected (ND) to 59 ug/L, acetaldehyde in the range of ND to 260 ug/L, propionaldehyde in the range of ND to 0.9 ug/L, and N-butyraldehyde ND to 0.3 ug/L. It is noteworthy that formaldehyde was observed at 59 ug/L in one sample, which is close to the Japanese limit of 80 ug/L. Acetaldehyde was detected in 19 out of 24 samples of bottled mineral water and 13 of these samples exceeded acetaldehyde concentrations of 100 ug/L.

Dong M, DeEdwardo AH, Zitomer F. Determination of residual acetaldehyde in polyethylene terephthalate bottles, preforms, and resins by automated headspace gas chromatography. Journal of Chromatographic Science. (1980) 18: 242-246.

Acetaldehyde analysis of PET bottles and resins is important because small amounts acetaldehyde can affect beverage taste. This study describes a rapid and sensitive method for determining residual acetaldehyde in PET resins, preforms, and bottles using automated headspace gas chromatography.

Acetaldehyde levels ranged from 0.5 to 6.0 ppm for commercial resin, from 30 to 60 ppm for amorphous resin, and from 6 to 24 ppm for preforms and bottles. The author states that since only a limited number of lots were examined, these data may not be representative of the actual acetaldehyde levels in commercial PET bottles. Also worth noting is that this study analyzed the PET directly rather than analyzing the leaching into the beverages.

Table A. 1 Summary of compounds detected in beverages in acetaldehyde studies from PET bottles

Compound	Storage Time	Temperature (°C)	Concentration (ppb)	Reference
Acetaldehyde	0 day		18.5 – 358.5	Ozlum 2008
	2 months	5	17 – 3150	Ozlum 2008
		20	16.5 – 8100	Ozlum 2008
		40	273.5 – 53000	Ozlum 2008
	6 months	5	10 – 10530	Ozlum 2008
		20	28 – 45195	Ozlum 2008
		40	1630 – 130000	Ozlum 2008
			0.4 – 1.1	Choodum et al. 2007
			100	Nijssen et al. 1996
	12 weeks	20	39 – 40	Nijssen et al. 1996
	12 weeks	30	58 – 61	Nijssen et al. 1996
	170 day	Room temp	78	Dabrowska et al. 2003
		44.3 – 107.8	Mutsuga et al. 2006	
		35.9 – 46.9		
		41.4 – 44.8		
		0.9 – 317.8	Nawrocki et al. 2006	
Formaldehyde	170 days	Room Temp	760	Dabrowska et al. 2003
			10.2 – 27.9	Mutsuga et al. 2006
			7.4 – 13.7	
			13.6 – 19.5	
			2.2 – 96.1	
Acetone			5.1 – 125.6	Nawrocki et al. 2002

Overview of Antimony Studies

In 90 percent of manufactured PET, antimony trioxide (SB₂O₃) is used as a catalyst for the reaction of terephthalic acid and ethylene glycol (Westerhoff et al. 2008). Antimony trioxide has been classified as “possibly carcinogenic to humans (Group 2B)” (International Agency for Research Center on Cancer 1989) and as a priority pollutant by the U.S. EPA, the European Union, and the German Research Foundation (Shotyky et al. 2006).

The following are antimony threshold guidelines commonly recommended for drinking water:

- World Health Organization 20 µg/L
- U.S. EPA 6 µg/L
- Health Canada 6 µg/L
- German Federal Ministry of Environment 5 µg/L
- Japan 2 µg/L

Antimony is a regulated drinking contaminant since exposure can result in health effects such as nausea, vomiting, and diarrhea when exposure to concentrations exceeds the maximum concentration level (MCL) for short periods. Long-term exposure can result in increased blood cholesterol and decreased blood sugar (Westerhoff et al. 2008).

Antimony Study Summaries

Shotyky W, Krachler M, Chen B. Contamination of Canadian and European bottled waters with antimony from PET containers. Journal of Environmental Monitoring. (2006) 8: 288-292.

Shotyky et al. conducted a study to determine if antimony concentrations that have been reported in literature are simply a reflection of concentrations in the bottled water from different regions or if the bottled water has been contaminated by the PET bottles. This study found that antimony leached from PET bottles into beverages. Antimony was found in 15 brands of Canadian bottled water and 48 European brands. Twelve brands of natural water bottled in PET from Canada contained 156 + 86 ng/L antimony and three brands of deionized water contained 162 + 30 ng/L antimony. A comparison of three German brands of bottled water sold in both glass and PET bottles showed that the water bottled in PET contained up to 30 times more antimony than the water bottled in glass. To verify that the antimony in the water was leaching from PET bottles, water was collected into LDPE bottles from a German commercial source prior to bottling. This water contained 3.8 + 0.9 ng/L antimony versus the same water bottled in PET containers containing 359 + 54 ng/L. After three storage months at room temperature, this same water bottled in PET 0 contained 626 + 15 ng/L antimony. Other German brands of PET bottled water contained 253 - 546 ng/L antimony. The mean concentration of antimony was 343 n/L from 35 brands of water from 11 European countries. Another test to verify antimony leaching from PET took pristine Canadian water (containing 2.2 ng/L antimony) and bottled it in PET bottles from Germany. This water contained 50 + 17 ng/L after 37 days and 566 ng/L after six months of storage at room temperature. The concentrations of antimony found in this study are all below acceptable drinking water standards in these countries.

Shotyk W, Krachler M. Contamination of bottled waters with antimony leaching from polyethylene terephthalate (PET) increases upon storage. Environmental Science & Technology. (2007) 41: 1560-1563.

In another study conducted by Shotyk and Krachler, antimony concentrations were measured from 132 brands of bottled water from 28 countries. The amount of antimony measured in two of the brands were above the maximum allowable level in Japan (2 µg/L). In the 14 water brands from Canada, the antimony concentration increased 19 percent over a six-month storage time at room temperature. In 48 brands of water from Europe, the antimony concentrations increased an average of 90 percent under the same conditions. One mineral water from France, purchased in Germany, yielded an antimony concentration of 725 ng/L when first tested, but subsequently yielded 1,510 ng/L after six months of storage. The same brand of water purchased in Hong Kong yielded an antimony concentration of 1,990 ng/L. Tap water in Germany that was bottled commercially in PET in December 2005 contained 450 + 56 ng/L of antimony versus 70.0 + 0.3 ng/L when sampled from a household faucet in the same German village.

Westerhoff P, Prapaipong P, Shock E, Hillaireau A. Antimony leaching from polyethylene terephthalate (PET) plastic use for bottled drinking water. Water Research. (2008) 42: 551-556.

The researchers purchased nine commercial bottled waters in Arizona. These water samples were tested for antimony concentrations, as well as for the potential to release antimony from the plastic to the water. For comparison, local Arizona tap water was analyzed and found to contain 0.146 + 0.002 ppb antimony. Antimony concentrations in the bottled waters ranged from 0.095 – 0.521 ppb at the beginning of the study. After three months stored at 22 °C there was no statistically significant increase in antimony concentration. However, storage at higher temperatures had a significant effect on antimony concentrations in the bottled water. Water bottles stored for seven days at 80 °C, reached an antimony concentration of 14.4 ppm (more than twice the U.S. EPA MCL). For exposure temperatures of 60, 65, 70, 75, 80, and 85 °C, the exposure period that exceeded the 6 ppb MCL were determined to be 176, 38, 12, 4.7, 2.3, and 1.3 days respectively. The results of this study also indicate that temperature, rather than sunlight exposure, appears to direct antimony leaching from PET water bottles. The leaching rate is low when storage temperatures are below 60°C, but when storage temperatures are above 60 °C, leaching occurs rapidly. In the southwestern U.S., temperatures inside garages and automobiles where bottled water is often stored can exceed 60 °C. Microwave digestion of PET bottle of one brand revealed the bottle contained 213 + 35 mg/kg of antimony.

Table A. 2 Summary of Compounds Detected in Beverages in Antimony Studies from PET Bottles

Compound	Storage Time	Temperature (°C)	Source	Water type	Conc. (ppb)	Reference
Antimony	0 day		Canada	Natural	112 – 375	Shotyk et al. 2006
			Canada	Deionized	134 – 195	Shotyk et al. 2006
			Germany	Natural	359 ± 54	Shotyk et al. 2006
	3 month	Room Temp	Germany	Natural	626 ± 15	Shotyk et al. 2006
			Germany	Natural	253 – 546	Shotyk et al. 2006
			Europe	Natural	343	
	37 day	Refrigerated	Germany	Natural	59 ± 17	
	6 month	Room Temp	Germany	Natural	556	
	6 month	Room Temp	16 Countries		0.0089 – 2.570	Shotyk & Krachler 2007
	6 month	Room Temp	Japan		0.0009 – 1.520	Shotyk & Krachler 2007

Overview of Oligomer Studies

PET contains small amounts of low molecular weight oligomers which mainly consist of cyclic compounds ranging from dimer to pentamer (Castle 1980). PET packaging may contain low levels of residual monomer and low molecular weight oligomers which are formed during the resin polymerization and melting process in addition to additives, reaction by-products, and polymer degradation products (Nassar et al. 2005). The main oligomers of PET are the cyclic oligomers (dimer to nonamer) besides the linear oligomers (Nassar et al. 2005). The cyclic trimer has been shown to migrate and represents 98 percent of all surface oligomers in PET (Besnoin et al. 1989).

Oligomer Study Summaries

Castle L, Mayo A, Crews C, Gilbert J. Migration of poly(ethylene terephthalate) (PET) oligomers from PET plastics into foods during microwave and conventional cooking and into bottled beverages. Journal of Food Protection. (1980) 52(5): 337-342.

This study detected very low levels of the migration of oligomers into beverages bottled in PET. A variety of drinks were analyzed including soda, carbonated water, and mineral spirits. Migration into all beverages were either non-detectable or barely above the limit of detection (0.05 mg/kg).

Nassar ALM, Lopes LMX, Eberlin MN, Monteiro M. Identification of oligomers in polyethyleneterephthalate bottles for mineral water and fruit juice. Development and validation of a high-performance liquid chromatographic method for the

determination of first series cyclic trimer. Journal of Chromatography A. (2005) 1097: 130-137.

This study aimed to identify oligomers in PET bottles used for mineral water and fruit juice and to develop and validate an analytical method to determine first series cyclic trimer oligomers in PET bottles. Oligomers were extracted and analyzed from PET bottles supplied by Brazilian beverage companies. Cyclic oligomers were identified in four bottles used for mineral water and two used for fruit juice using high performance liquid chromatography (HPLC), mass spectroscopy (MS), and ¹H and ¹³C nuclear magnetic resonance spectroscopy (NMR) data. The first series cyclic trimer was the predominant oligomer detected. The concentrations of the first series of cyclic trimer in the PET bottles ranged from 300 to 462 mg/100g. The first series cyclic tetramer, the first series cyclic dimer, and the second series cyclic trimer were also detected, but not quantified. See Figure 1 for oligomer structures.

Terephthalic Acid and Terephthaloyl Moieties Study Summaries

Begley TH, Hollifield HC. Liquid chromatographic determination of residual reactants and reaction by-products in polyethylene terephthalate. Journal - Association of Official Analytical Chemists. (1989) 72(3): 468-470.

Begley and Hollifield demonstrated an analytical method to measure several low molecular weight moieties in PET including terephthalic acid, bis(2-hydroxyethyl), terephthalate (BHET), monohydroxy ethylene terephthalic acid (MHET), and cyclic tris(ethylene terephthalate). However, this study only analyzed the concentrations directly in PET film and not the potential for leaching from containers into food or beverages.

Tice PA, McGuinness JD. Migration from food contact plastics. Part I. Establishment and aims of the PIRA project. Food Additives and Contaminants. (1987) 4(3): 267-276.

This study developed an analytical method to identify and quantify terephthalic acid and isophthalic acid in plastics, food simulants, and food. Tice and McGuinness measured 0.02 mg/kg (20 ppb) of terephthalic acid in 50 percent ethanol bottled in PET and 0.03 mg/kg (30 ppb) in vodka bottled in PET.

Overview of Ethylene Glycol

PET is prepared by the reaction of ethylene glycol with either terephthalic acid or dimethyl terephthalate. PET is used in bottling because it is an effective barrier against carbon dioxide loss (Kashtock and Breder 1980).

Ingestion of ethylene glycol has been shown to cause intoxication and mild gastritis. Ethylene glycol poisoning presents in three fairly distinct stages: central nervous system effects, cardiopulmonary effects, and renal failure. Ethylene glycol itself has low toxicity. However, it is metabolized to several toxic metabolites such as glycolaldehyde, glycolic acid, glyoxalic acid, and oxalic acid. These metabolites can cause acidosis, renal failure, and death after a delay of 4 to 12 hours (Morelli-Cardoso et al. 1997).

A specific migration limit of 30 mg/kg (30 ppm) is permitted in foods or food simulants in the European Community and in Brazil (Morelli-Cardoso et al. 1997).

Ethylene Glycol Study Summaries

Kashtock M, Charles VB. Migration of ethylene glycol from polyethylene terephthalate bottles into 3% acetic acid. Journal - Association of Official Analytical Chemists. (1980) 63(2): 168-172.

Ethylene glycol migration from PET bottles into the food stimulant 3 percent acetic acid was evaluated using 32-fluid-ounce bottles. The bottles were filled with 3 percent acetic acid and were stored at 32°C for six months. The FDA recommends 3 percent acetic acid as a food stimulant for carbonated beverages of pH 5.0 or below. The final concentration of ethylene glycol in the 3 percent acetic acid solution was approximately 100 ppb by the sixth month.

Approximately 2 ppm ethylene glycol in the bottle wall would have been required to account for 100 ppb ethylene glycol, which migrated from the bottle walls into the solution. Three separate unused PET bottles were ground and exhaustively extracted with methylene chloride for three days. An ethylene glycol equivalent of approximately 15 ppm from the bottle material was found in the extract from the PET bottle walls.

Morelli-Cardoso MHW, Tabak D, Cardoso JN, Pereira AS, Abrantes S. Application of capillary gas chromatography to the determination of ethylene glycol migration from PET bottles in Brazil. Journal of High Resolution Chromatography. (1997) 20: 183-184.

This study undertook a specific migration study with virgin PET bottles and aqueous food simulants: distilled water, 3 percent w/v aqueous acetic acid, and 15 percent v/v aqueous ethanol. There were 48 PET bottles analyzed. Three sets of 16 PET bottles were analyzed, with each set corresponding to one of the three simulants. The limit of detection for this study was 5 mg/kg. The study detected no migration of ethylene glycol.

Based on this ethylene glycol migration study, the authors state the PET bottles produced by the Brazilian companies are of good quality. It is worth noting that this study did not contain any quantitative data regarding ethylene glycol detection or non-detection from the analysis.

Appendix B: Literature Review: Tentative Target Compound List for PET, PLA, PHA Chemical Migration Study

The following tables were compiled from literature review; FDA Food Contact Notification Database; and Contaminant Levels in Recycled PET Plastic (Konkol, 2007, see pp. 5-30 (section 2.2)). These compounds are only listed as potential candidates for migration from plastic to water.

Table A. 3. Compounds used in the manufacture of PET

Compound	Identification Category	Research Study Information	Manufacturing Process Information
(BHET) - bis-(2-hydroxyethyl)terephthalate			
(BHT)- 2,6-bis(1,1-dimethylethyl)-4-methylphenol			
(DBP) - Dibutyl phthalate			
(DEHP) - Bis(2-ethylhexyl)phthalate			
(DEP) - Diethyl phthalate			
(MHET) monohydroxyethylene terephthalic acid			
2-[4-(1,1-dimethylethyl)-2-methylpennoxy]-ethanol			
2-methyl-1,3-dioxolan			
2-phenyl-1,3-dioxolan			
acetaldehyde	Shown to migrate into beverage from PET	Beverage Container Leaching Research	Byproduct of high temperature process such as injection molding of PET
adipate (BEHA) - di-(2-ethylhexyl)phthalate			
antimony	Shown to migrate into beverages from PET	Beverage Container Leaching Research	Catalyst in the manufacturing process of PET
Antimony acetate			Catalyst in the manufacturing process of PET
Antimony trioxide			Catalyst in the manufacturing process of PET
benzaldehyde			
benzoic acid butyl ester			
BHA - benzyl hexyl adipate			
bis-1,1'-(1,2-ethenediyl)-benzene			

Compound	Identification Category	Research Study Information	Manufacturing Process Information
butoxybenzene			
cadmium	Potential migrants of PET		Catalyst in manufacturing process of PET; Catalyst used in transesterification step of Dimethyl terephthalate with Ethylene Glycol
carbodiimide			Antioxidant
Cobalt	Potential migrants of PET	Identified in food simulants	Catalyst in manufacturing process of PET; Catalyst used in transesterification step of Dimethyl terephthalate with Ethylene Glycol
cobaltous chloride			Toner
cobaltous nitrate			Toner
cyclic dimer			
cyclic dimer ether			
cyclic trimer	Shown to migrate into beverages from PET	Beverage Container Leaching Research	
decamethyl-cyclopentasiloxane			
dibenzoate-1,2-ethanediol			
DiBP - Diisobutyl phthalate			
dibutylthioamine zinc formate			Antioxidant
dicarboxyl acid			
Dicarboxyl acid comprises Terephthalic acid (PTA), Isophthalic acid (IPA), Dimethyl terephthalate (DMT), 2,6-			

Compound	Identification Category	Research Study Information	Manufacturing Process Information
naphthalenedicarboxylic acid			
<p>dihydric alcohol</p> <p>Dihydric alcohol comprises Ethylene glycol, propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,4-cyclohexanedimethanol (CHDM).</p>			
Dimer			
dimer ether			
dimethyl cyclohexane-1,4-dicarboxylate			
dimethyl terephthalate	Potential migrants of PET		Starting compound in the manufacture of PET
DiOP - DIISOCTYL PHTHALATE			
DOA - dioctyl adipate			
dodecanoic acid			
erucamide			
ethylene glycol	Shown to migrate into beverages from PET	Beverage Container Leaching Research; identified in bottle walls	Starting compound in the manufacture of PET
germanium			Catalyst in manufacturing process of PET; alternative to antimony
germanium dioxide			Catalyst in manufacturing process of PET; alternative to antimony
hexamethyl-cyclotrisiloxane			

Compound	Identification Category	Research Study Information	Manufacturing Process Information
isoquinoline			
Lead	Potential migrants of PET		Catalyst used in transesterification step of Dimethyl terephthalate with Ethylene Glycol
manganese	Potential migrants of PET		Catalyst in manufacturing process of Ethylene Glycol; Catalyst used in transesterification step of Dimethyl terephthalate with Ethylene Glycol
manganese acetate			Catalyst
methanol			
methyl vinyl ester terephthalic acid			
octamethyl-cyclotetrasiloxane			
oleamide			
phosphoric acid			Stabilizer additive
phosphorous acid			Stabilizer additive
p-terephthalate monomethyl ester	Potential migrants of PET		Intermediate in the manufacture of Dimethyl Terephthalate
p-toluic acid	Potential migrants of PET		Intermediate in the manufacture of Dimethyl Terephthalate
p-toluic acid methyl ester	Potential migrants of PET		Intermediate in the manufacture of Dimethyl Terephthalate
p-xylene	Potential migrants of PET	Compound released from roasting bag or susceptor film	Used in the manufacture of Terephthalic Acid and Dimethyl Terephthalate
Silver	Potential migrants of PET		Catalyst in manufacturing process of Ethylene Glycol
Silicon dioxide	Potential migrant of PET		Used as an amorphous plasma-deposited silicon coating on the food-contact surface of

Compound	Identification Category	Research Study Information	Manufacturing Process Information
			polyethylene terephthalate (PET) food packaging articles
salicyl cobaltous salicylate			Toner
terephthalic acid	Shown to migrate into beverages from PET	Beverage Container Leaching Research; identified in bottle walls	Starting material in PET manufacture
tetrahydrated cobaltous acetate			Toner
Thioether			Antioxidant
Tinuvin P - 2-(2-hydroxy-5-methylphenyl)benzotriazole			
Titanium			
titanium nitride			Additive in food-contact polyethylene terephthalate (PET) bottles
Toluene	Substance released from heated PET bottle	Heated PET bottle research; bottled heated to 150 C; VOCs released from PET were analyzed by GC/MS	Catalyst used in transesterification step of Dimethyl terephthalate with Ethylene Glycol
triethyl phosphate			Stabilizer additive
trimethyl phosphate			Stabilizer additive
triphenyl phosphate			Stabilizer additive
Zinc			
zinc acetate			

Table A. 4. Compounds determined by the Environmental Working Group from the FDA Food Contact Notification website

Chemical	CAS number	Other names
2-Cyano-3,3-diphenyl-2-propenoic acid 2-ethylhexyl ester	6197-30-4	Octocrylene
Phenol,2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-	103597-45-1	Bisotrizole Tinosorb M
Diethyl 3,5-di-tert-butyl-4 hydroxybenzylphosphonate	976-56-7	Irganox 1222
(2-(2H-benzotriazol-2-yl)-4-(1,1,3,3,-tetramethylbutyl)phenol	3147-75-9	Octrizole
2,3-Dihydro-2-methyl-4(1H)-quinazolinone	54764-01-1	dihydro version of 2-Methyl-4(3H)-quinazolinone CAS 1769-24-0
1,3-Cyclohexanedicarboxylic acid (CHDA)	3971-31-1	
1H-benz[de]isoquinoline-1,3(2H)-dione, 2-[2,6-bis(1-methylethyl)phenyl]-6-[4-(1,1,3,3-tetramethylbutyl)phenoxy]	852282-89-4	new antioxidant, marketed as Uvinul S-Pack, can buy standards from BASF?
Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)	70321-86-7	
Calcium bis[monoethyl(3,5-di-tert-butyl-4-hydroxy-benzyl)phosphonate]	65140-91-2	structurally related to irganox1222
Carbethoxymethyl diethyl phosphonate	867-13-0	Triethyl phosphonoacetate
2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-hexyloxy)phenol	147315-50-2	
2,2'-Ethylidenebis(4,6-di-tert-butylphenyl)fluorophosphonite	118337-09-0	
Tris(2,4-ditert-butylphenyl) phosphite and its corresponding phosphate	31570-04-4	Irgafos 168
Dimethyl 5-sulphoisophthalate	138-25-0	

Chemical	CAS number	Other names
5-Sulfoisophthalic acid	22326-31-4	
Hydroxyethylidine- 1,1 -diphosphonic acid	2809-21-4	Etidronic acid
2-Aminobenzamide	88-68-6	
Dimethylterephthalate (DMT), 1,4-benzenedicarboxylic acid, dimethyl ester	120-61-6	
Terephthalic acid (TPA), 1,4-benzenedicarboxylic acid)	100-21-0	
Isophthalic acid (IPA)	121-91-5	
Monomethyl terephthalate	1679-64-7	
Bis-(1,4-hydroxyethyl) terephthalate (BHET)	959-26-2	
Pyromellitic dianhydride (PMDA)	89-32-7	
Pyromellitic acid	89-05-4	
Trimellitic anhydride	552-30-7	
1,4-cyclohexanedimethanol (CHDM)	105-08-8	
2,6-naphthalenedicarboxylic acid (NDCA)	1141-38-4	
Dimethyl 2,6-naphthalenedicarboxylate		
2,6-naphthalenedicarboxylic acid, dimethyl ester (NDCE	840-65-3	
Benzophenone (BP)	119-61-9	
Benzophenone imine (BPI)	1013-88-3	

Chemical	CAS number	Other names
m-Toluic acid (mTA)	99-04-7	
3-Carboxybenzaldehyde (CBA)	619-21-6	
Benzoic acid (BA)	65-85-0	
2-cyanoacetic acid ethyl hexyl ester (CAEHE)	13361-34-7	
Isatoic anhydride	118-48-9	
Anthranilic acid	118-92-3	
Ethyl anthranilate (EA)	87-25-2	
2(2'-Hydroxy-5'-methylphenyl)benzotriazole	2440-22-4	Drometrizole, Tinuvin P
Butylated hydroxytoluene	128-37-0	BHT
Pentaerythritol, tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)	6683-19-8	Irganox 1010
Hydrocinnamic acid, 3,5-di-t-butyl-4-hydroxy-, octadecyl ester	2082-79-3	Irganox 1076
2,6-di-tert-4-(methyl-amino methyl)-phenol)	88-27-7	Ethyl 703
2,6-Di-tert-butylphenol (DTBP)	128-39-2	Ethyl 701
4-tert-octylphenol	140-66-9	
Limonene	138-86-3	Flavor agent, marker of recycled PET
Methyl salicylate	119-36-8	
2-Methylnaphthalene	91-57-6	
Hexamethylcyclotrisiloxane	541-05-9	D3

Chemical	CAS number	Other names
Octamethylcyclotetrasiloxane	556-67-2	D4
Decamethylcyclopentasiloxane	541-02-6	D5
N-methylpyrrolidone	872-50-4	
Erucyl amide	112-84-5	Erucamide
1,3-Benzenedimethanamine	1477-55-0	
1,6-Diaminohexane	124-09-4	Hexamethylenediamine
Benzaldehyde	100-52-7	
Butoxybenzene	1126-79-0	
2-Phenyl-1,3-dioxolane	936-51-6	
2-Methyl-1,3-dioxolane	497-26-7	
Dimethyl hexahydroterephthalate	94-60-0	Dimethyl cyclohexane-1,4-dicarboxylate
2-butoxyethanol	111-76-2	
Adipic acid	124-04-9	

Table A. 5. Compounds used in the manufacture of PLA

Compounds	Trade Names	Information
lactic acid (2-hydroxypropionic acid)		Starting material; potential degradation byproduct
D-lactide		Starting material; potential degradation byproduct
L-lactide		Starting material; potential degradation byproduct
polylactide polymer		Starting material; potential degradation byproduct
Lactate		Potential degradation byproduct or intermediate
pyruvate		
lactate dehydrogenase		Potential degradation byproduct or intermediate
tricarboxylic acid		Potential degradation byproduct or intermediate
acetic acid		Potential degradation byproduct or intermediate
pyruvic acid.		
glucose		
	Lapol	Plasticizer in PLA
	Biomax Thermal 300	Heat stabilizing modifier for thermoformed packaging
	Biostrength 900	Acrylic copolymer that is said to enable more consistent processing of PLA

Compounds	Trade Names	Information
	Biostrength 130 additives	Improves impact strength; for clarity applications
	Biostrength 150 additives	Improves impact strength; for opacity applications
	Biostrength 700 acrylic copolymer	Improves melt strength and enhances processability at levels of one percent to four percent
calcium carbonate	EMforce Bio	Reduces brittleness; filler
Calcium sulfate (dehydrated gypsum)		
polyhydroxybutyrate valerate (PHBV)		Reduces brittleness; improves heat resistance
silica		Increases toughness; maintains clarity
poly[(3-hydroxybutyrate)-co-(3-hydroxyhexanoate)] (PHBHHx)		Improves toughness
benzophenone		possible additive
acrylamide		possible additive
acrylic acid		possible additive
	Paraloid BPM-500	Impact modifier; designed to improve impact strength and tear resistance of PLA without sacrificing clarity; uses nanoparticles
acrylic-based melt strength enhancers		Improves fabrication performance for foamed PLA
	Biomax Strong 120	Ethylene copolymers that improve impact strength and toughness of both amorphous

Compounds	Trade Names	Information
		and crystalline PLA
	Biomax Strong 100	Developed to toughen PLA; also acts as processing aids that significantly reduce screw torque and improve melt stability
	Biomax Thermal 120	A proprietary heat-distortion modifier that will allow PLA thermoformed parts to withstand hot transport and storage.
	Elvaloy copolymers	Processing aids to help various types of biopolymers feed better during injection molding
an epoxy-functional styrene/acrylic oligomer	CESA-Extend	Improves melt strength and increases tensile strength properties
Hydrocerol endothermic foaming agent		To enhance melt strength for foams and other applications,
		Bio-based UV-stabilizer master batches that protect the contents of transparent biopolymer packaging.
Renol-natur color concentrates		Derived mainly from plants and include red, orange, yellow and green, with blue in the final stages of development. They have excellent clarity, though their light fastness is not as high as traditional colorants.
	Ecoflex	Adds melt strength and flexibility

Compounds	Trade Names	Information
	Rejuven8 Plus	Made from 95 per cent PLA; is said to work well in most thermoforming processes. "The unique alloy material has performance enhanced physical properties over standard PLA with impact properties similar to PET, and also raises the heat resistance properties to well over 70°C
methylene-diisocyanate (MDI)		Coupling agent; MDI is recognized as a toxic substance, however further studies are required to assess the problems that could occur if MDI entered the environment.
Glycerol		Plasticizer
Sorbitol		Plasticizer
Propylene glycol		Plasticizer
Polyethylene glycol		Plasticizer
Triethyl citrate		Plasticizer
Triacetine		Plasticizer
Ethylene glycol		Plasticizer. Ethylene glycol, however, is a recognized environmental pollutant. Direct exposure to the compound can cause skin and eye damage in humans, with a lethal dose if ingested of 100mL. The lethal concentration for fish has been found to be 100mg/L. (Material Safety Data Sheet – Ethylene Glycol, 2001).
silicon dioxide		filler
titanium dioxide		filler

Compounds	Trade Names	Information
Tin		Catalyst
		slip and antiblock concentrates
		A line of custom color master batches for a wide range of biopolymers. They are formulated from sustainable sources, including primarily organic-based pigments.
	OnCap Bio line	A range of impact-modifier master batches, for opaque and transparent biopolymer systems. PolyOne continues to explore technologies to enhance the heat resistance of bio-based resins, particularly PLA and starch blends. It has developed polymer blends containing PLA that can raise the HDT from around 70 degree C to around 90 degree C. However, the non-PLA blend components are neither bio-derived nor biodegradable, and the system is opaque.
		Bio-based UV-stabilizer master batches that protect the contents of transparent biopolymer packaging.
	OnColor Bio	Color concentrates and liquid colorants are based in part on sustainable raw materials. The concentrates use biopolymer carriers such as PLA, PHA, modified starch compounds and biodegradable polyesters. Opaque colors are available for all these biopolymers, but transparent colors are also available for PLA.
Stannous octoate		Catalyst for ring-opening polymerization of PLA
Octoate		Catalyst for ring-opening polymerization of PLA

Compounds	Trade Names	Information
metal halides		Catalyst for ring-opening polymerization of PLA
carboxylates		Catalyst for ring-opening polymerization of PLA
Oxides		Catalyst for ring-opening polymerization of PLA
Metal alkoxides (Mg, Sn, Ti, Zr, Zn, and Al-alkoxides)		Catalyst for ring-opening polymerization of PLA
magnesium oxide		Catalyst for ring-opening polymerization of PLA
tin oxide		Catalyst for ring-opening polymerization of PLA
titanium oxide		Catalyst for ring-opening polymerization of PLA
zirconium oxide		Catalyst for ring-opening polymerization of PLA
zinc oxide		Catalyst for ring-opening polymerization of PLA
aluminum oxide		Catalyst for ring-opening polymerization of PLA
	Mecostat-3/725	Anti-fog agent; external topical coatings
	Mecostat-3/723	Anti-fog agent; external topical coatings
	PETAFD-20	Anti-fog agent; external topical coatings

Compounds	Trade Names	Information
	ELECUT C-031L	Anti-fog agent; external topical coatings; pending FDA approval
		Anti-fog agent; internal agents
		Anti-fog agent; internal agents
		Anti-fog agent; internal agents
oligomeric lactic acid (OLA)		plasticizer
citrate ester		plasticizer
poly(butylene terephthalate)	Hytrel TM 4056	elastomer; poly(butylene terephthalate) and polyether glycol
polyether glycol	Hytrel TM 4056	elastomer; poly(butylene terephthalate) and polyether glycol
glycolide		plasticizer
poly(glycolic acid)		plasticizer
caprolactone		plasticizer
valerolactone		plasticizer
styrene-butadiene		co-polymer
polyisoprene (natural rubber)		
styrene-isoprene-styrene block copolymers		
acrylonitrile-butadiene-styrene block copolymers		
styrene-ethylene-styrene block copolymers		
propylene-ethylene-propylene block copolymers		

Compounds	Trade Names	Information
propylene-isoprene-propylene block copolymers		
Flax		fiber
Kenaf		fiber
glass fiber		fiber
wood fiber		fiber
Mica		filler; increase the modulus of PLA with 10-30% added.
Kaolin (clay; $Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$)		filler
glass (milled/flaked)		filler
variety of inorganic carbonates and sulfates,		filler
Starch		filler
Talc		filler; increase the modulus of PLA with 10-30% added; acts as a nucleator
Maleic anhydride		compatibilizing polymer
polyvinyl alcohol		Improves heat resistance
cellulose		Improves heat resistance
Walnut shell flour		Improves heat resistance
pine wood flour		flame retardant
(silanes/titanates) metal hydroxides		
Synthetic silicate		
levulinic ketals		

Compounds	Trade Names	Information
Decanedioic acid polymer with 2-hydroxypropanoic acid and 1,2-propanediol, block (CAS Reg. No. 329223-54-3)		Used as a modifier in the manufacture of polylactide (PLA) polymers for single-use food-contact articles; for use at levels not to exceed 20 weight percent in PLA polymers in contact food types
styrene		Polymeric chain extender; shall be used at a maximum level of 0.2 percent by weight of polylactide polymers; shall be used at a maximum level of 1.2 percent by weight of foamed polylactide polymers; may contact all food types (except >15 percent alcohol); notification submitted jointly by BASF and NatureWorks
methyl methacrylate		Polymeric chain extender; shall be used at a maximum level of 0.2 percent by weight of polylactide polymers; shall be used at a maximum level of 1.2 percent by weight of foamed polylactide polymers; may contact all food types (except >15 percent alcohol); notification submitted jointly by BASF and NatureWorks
glycidyl methacrylate		Polymeric chain extender; shall be used at a maximum level of 0.2 percent by weight of polylactide polymers; shall be used at a maximum level of 1.2 percent by weight of foamed polylactide polymers; may contact all food types (except >15 percent alcohol); notification submitted jointly by BASF and NatureWorks

Table A. 6. Compounds used in the manufacture of PHA

Compounds	Trade Name	Information
poly-3-hydroxyoctanoate (PHO)		Resin
poly-3-hydroxybutyrate-co-3-hydroxyvalerate		Resin
poly-3-hydroxybutyrate-co-3-hydroxypropionate		Resin
poly-3-hydroxybutyrate-co-4-hydroxyvalerate		Resin
poly-3-hydroxybutyrate-co-4-hydroxybutyrate		Resin
poly-3-hydroxybutyrate-co-3-hydroxyhexanoate		Resin
poly-3-hydroxybutyrate-co-3-hydroxyoctanoate		Resin
poly-4-hydroxybutyrate		Resin
poly-3-hydroxypropionate		Resin
poly-4-hydroxyvalerate		Resin
methanol		Carbon substrate
acetic acid		Carbon substrate
propionic acid		Carbon substrate
butyric acid		Carbon substrate
lactic acids		Carbon substrate
lauric acid		Carbon substrate

Compounds	Trade Name	Information
oleic acid		Carbon substrate
levulinic acid		Carbon substrate
octanoic acid		Carbon substrate
anatoxin-a		cyanotoxins
anatoxin-as		cyanotoxins
aplysiatoxin		cyanotoxins
cyllindrospermopsin		cyanotoxins
domoic acid		cyanotoxins
microcystin LR		cyanotoxins
nodularin R (from Nodularia		cyanotoxins
saxitoxin		cyanotoxins
(R)-3-hydroxybutyric acid		bacterial fermentation
acetyl-coenzyme-A		
1,5-Pentenediol		Carbon Substrate
raffinose		Carbon Substrate
Glucose		Carbon Substrate
sucrose		Carbon Substrate
fructose		Carbon Substrate
γ -Butyrolactone,		Carbon Substrate
1,4-Butanediol,		Carbon Substrate
1,6-Hexanediol		Carbon Substrate

Compounds	Trade Name	Information
ϵ -caprolactone		Carbon Substrate
Xylose		Carbon Substrate
Adonitol		Carbon Substrate
arabinose		Carbon Substrate
arabitol		Carbon Substrate
cellobiose		Carbon Substrate
lactose		Carbon Substrate
maltose		Carbon Substrate
melibiose		Carbon Substrate
rhamnose		Carbon Substrate
Xylitol		Carbon Substrate
trehalose		Carbon Substrate
sorbitol		Carbon Substrate
galactose		Carbon Substrate
mannitol		Carbon Substrate
pyruvate		Carbon Substrate
glutamate		Carbon Substrate
Valeric acid		Carbon Substrate
Decanoic acid		Carbon Substrate
4-hydroxybutyric acid		Carbon Substrate
maltose		Carbon Substrate

Compounds	Trade Name	Information
maltotetraose		Carbon Substrate
maltohexaose		Carbon Substrate
Nonanoic acid		Carbon Substrate
Ribulose monophosphate (RMP)		Carbon Substrate
Pentanol		Carbon Substrate
n-Octane		Carbon Substrate
Octanoate		Carbon Substrate
undecenoic acid		Carbon Substrate
Sodium gluconate		Carbon Substrate
3-Hydroxypropionic acid		Carbon Substrate
4-Hydroxybutyric acid		Carbon Substrate
butyric acid		Carbon Substrate
Zinc		Growth media
Iron		Growth media
Cl		Growth media
Co		Growth media
butyric acid		Growth media
CD		Growth media
CR		Growth media
CU		Growth media
Mn		Growth media

Compounds	Trade Name	Information
Mo		Growth media
Ni		Growth media
Sodium		Growth media
Calcium		Growth media
Mg		Growth media
Potassium		Growth media
chloroform		Extraction solvent
methylene chloride		Extraction solvent
propylene carbonate		Extraction solvent
dichloroethane		Extraction solvent
hypochlorite		Digestion
methanol		
ethanol		
potassium hydroxide (KOH)		Digest cellular material
sodium hypochlorite		PHA recovery
Sodium dodecylsulfate (SDS)		Digest cellular material
dioctylsulfosuccinate sodium salt [AOT]		Digest cellular material
hexadecyltrimethylammonium bromide [CTAB]		Digest cellular material
sodium dodecylsulfate [SDS]		Digest cellular material
polyoxyethylene-p-tert-octylphenol [Triton X-100]		Digest cellular material
polyoxyethylene(20)sorbitan monolaurate [Tween 20]		Digest cellular material

Compounds	Trade Name	Information
methyl formate		Extraction solvent
ethyl formate		Extraction solvent
propyl formate		Extraction solvent
butyl formate		Extraction solvent
isoamyl formate		Extraction solvent
pentyl formate		Extraction solvent
caproyl formate (or hexyl)		Extraction solvent
isopropyl propionate		Extraction solvent
isoamyl propionate		Extraction solvent
caproyl propionate (or hexyl)		Extraction solvent
methyl butyrate		Extraction solvent
propyl butyrate		Extraction solvent
isopropyl butyrate		Extraction solvent
isoamyl butyrate		Extraction solvent
pentyl butyrate (amyl)		Extraction solvent
caproyl butyrate (or hexyl)		Extraction solvent
methyl isobutyrate		Extraction solvent
ethyl isobutyrate		Extraction solvent
butyl isobutyrate		Extraction solvent
propyl isobutyrate		Extraction solvent
isopropyl isobutyrate		Extraction solvent

Compounds	Trade Name	Information
isoamyl isobutyrate		Extraction solvent
pentyl isobutyrate (amyl)		Extraction solvent
caproyl isobutyrate		Extraction solvent
propyl valerate		Extraction solvent
isopropyl valerate		Extraction solvent
butyl valerate		Extraction solvent
isobutyl valerate		Extraction solvent
isoamyl valerate (valerate of 3 -methyl-1-butyl)		Extraction solvent
pentyl valerate (amyl)		Extraction solvent
caproyl valerate (or hexyl)		Extraction solvent
methyl isoamylate (isovalerate) (3-methyl-1- methyl butanoate)		Extraction solvent
ethyl isoamylate (isovalerate) (3- methyl-1-ethyl butanoate)		Extraction solvent
propyl isoamylate (isovalerate) (3 -methyl-1-propyl butanoate)		Extraction solvent
isopropyl isoamylate (isovalerate) (3 -methyl-1-isopropyl butanoate)		Extraction solvent
butyl isoamylate (isovalerate) (3-methyl- 1-butyl butanoate)		Extraction solvent
isobutyl isoamylate (isovalerate) (3 -methyl -1-isobutyl butanoate)		Extraction solvent
isoamyl isoamylate (isovalerate) (3 -methyl -1-isoamyl butanoate)		Extraction solvent
pentyl isoamylate (isovalerate) (amyl) (3 -methyl-1-pentyl (amyl butanoate)		Extraction solvent

Compounds	Trade Name	Information
caproyl isoamylate (isovalerate) (hexyl		Extraction solvent
Ozone		Separation
calcium carbonate		filler
OnColor Bio		Color concentrates and liquid colorants are based in part on sustainable raw materials. The concentrates use biopolymer carriers such as PLA, PHA, modified starch compounds and biodegradable polyesters. Opaque colors are available for all these biopolymers, but transparent colors are also available for PLA.
citrate ester (triacetin)		plasticizer
levulinic ketals		

Appendix C: Measured Concentration of Organic Compounds in Water from Storage Experiment for each Bottle Type and Manufacturer

The names listed in the header of each table include all information about the condition being reported and take the form:

“PlasticType.ManufactureCode.TemperatureCondition_StorageCondition”.

For example, the name “PET.A.T1S0” indicates a PET bottle produced by manufacturer A stored at room temperature (T1 = room temperature, T2 = 35 C° and T3 = 50 C°) and for the overnight storage duration (S0 = overnight, S1 = 3 months and S2 = 6 months).

Each of the following tables lists results separately for each of the polymer type and manufacturer combinations.

Table A. 7. Storage Experiment Results for PET from Manufacture A

ChemName	PET.A.T1S0	PET.A.T1S1	PET.A.T2S1	PET.A.T3S1	PET.A.T1S2	PET.A.T2S2	PET.A.T3S2
2-Ethyl-3-methoxy-2-cyclopentenone		0.005	0.034	0.083	0.012	0.057	0.058
Benzothiazole				0.022		0.004	0.073
1,4-Dioxane-2,5-dione, 3,6-dimethyl-	0.071						
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-	0.074						
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone		0.054	0.175	0.727	0.201	0.354	0.848
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	0.002	0.012	0.029	0.460	0.162	0.258	1.021
4,6-di-tert-Butyl-m-cresol					0.017	0.033	0.078
Phenol, 2,4-bis(1,1-dimethylethyl)-			0.254	0.955	0.089	0.683	1.461
Diethyl Phthalate			0.087		0.076	0.022	
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-		0.019	0.034	0.060	0.019	0.018	0.056
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-	0.104	0.018	0.019	0.071			0.050
Benzophenone		0.012	0.138	0.785	0.030	0.399	1.285
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-		0.003	0.002	0.005	0.003	0.004	0.018
Phenol, 4-(1,1-dimethylpropyl)-		0.002	0.001	0.004	0.003	0.003	0.011
4-Methyl-2-tert-octylphenol		0.002	0.002	0.005	0.003	0.004	0.017
(52.583) unknown alkyl phenol				0.003	0.002	0.002	0.014
(52.648) unknown alkyl phenol		0.003	0.002	0.005	0.003	0.005	0.018
Phenol, 4-(1,1,3,3-tetramethylbutyl)-		0.006	0.004	0.016	0.006	0.007	0.062

ChemName	PET.A.T1S0	PET.A.T1S1	PET.A.T2S1	PET.A.T3S1	PET.A.T1S2	PET.A.T2S2	PET.A.T3S2
3,5-di-tert-Butyl-4-hydroxybenzaldehyde		0.021	0.093	0.288	0.065	0.193	0.611
Phenanthrene			0.006	0.109		0.025	0.318
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	0.100	0.026	0.358	0.292	0.217	0.461	0.262
Ethanone, 2,2-dimethoxy-1,2-diphenyl-			0.002	1.107	0.001	0.009	2.082
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester			0.005	0.001	0.001	0.005	
1-Methyldibenzothiophene				0.009	0.001	0.003	0.030
Dibutyl phthalate					0.553		
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione							
1-Propene-1,2,3-tricarboxylic acid, tributyl ester							
2,5-di-tert-Butyl-1,4-benzoquinone							
Tributyl acetylcitrate				0.001			0.006

Table A. 8 Storage Experiment Results for PET from Manufacture C

ChemName	PET.C.T1S0	PET.C.T1S1	PET.C.T2S1	PET.C.T3S1	PET.C.T1S2	PET.C.T2S2	PET.C.T3S2
2-Ethyl-3-methoxy-2-cyclopentenone			0.003	0.015		0.007	0.018
Benzothiazole				0.015			0.057
1,4-Dioxane-2,5-dione, 3,6-dimethyl-							
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-				0.003		0.001	
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone			0.002	0.028		0.006	0.062
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	0.002		0.010	0.427	0.087	0.219	1.652
4,6-di-tert-Butyl-m-cresol			0.011	0.018	0.060	0.037	0.088
Phenol, 2,4-bis(1,1-dimethylethyl)-				0.141			0.569
Diethyl Phthalate			0.097				
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-						0.003	0.022
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-	0.026						0.010
Benzophenone		0.011	0.010	0.331	0.007	0.039	0.751
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-	0.002	0.003	0.012	0.029	0.006	0.028	0.041
Phenol, 4-(1,1-dimethylpropyl)-		0.002	0.010	0.019	0.004	0.020	0.028
4-Methyl-2-tert-octylphenol	0.001	0.003	0.011	0.027	0.005	0.028	0.042
(52.583) unknown alkyl phenol		0.001	0.010	0.026	0.004	0.024	0.035
(52.648) unknown alkyl phenol	0.001	0.003	0.014	0.034	0.006	0.031	0.052
Phenol, 4-(1,1,3,3-tetramethylbutyl)-	0.003	0.006	0.027	0.074	0.012	0.062	0.109

ChemName	PET.C.T1S0	PET.C.T1S1	PET.C.T2S1	PET.C.T3S1	PET.C.T1S2	PET.C.T2S2	PET.C.T3S2
3,5-di-tert-Butyl-4-hydroxybenzaldehyde			0.016	0.304	0.046	0.108	0.882
Phenanthrene				0.025		0.003	0.132
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	0.256	0.023	0.033	0.130	0.068	0.210	0.172
Ethanone, 2,2-dimethoxy-1,2-diphenyl-				0.008	0.002	0.005	0.101
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester		0.013	0.059	0.017	0.036	0.093	0.015
1-Methyldibenzothiophene				0.002	0.001	0.002	0.013
Dibutyl phthalate	1.385					0.239	
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione							
1-Propene-1,2,3-tricarboxylic acid, tributyl ester							
2,5-di-tert-Butyl-1,4-benzoquinone				0.002	0.004		
Tributyl acetylcitrate			0.005				

Table A. 9. Storage Experiment Results for PET from Manufacture E

Compound	PET.E.T1S0	PET.E.T1S1	PET.E.T2S1	PET.E.T3S1	PET.E.T1S2	PET.E.T2S2	PET.E.T3S2
2-Ethyl-3-methoxy-2-cyclopentenone			0.000	0.007			0.005
Benzothiazole							0.019
1,4-Dioxane-2,5-dione, 3,6-dimethyl-							
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-							0.001
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone			0.003	0.019	0.002	0.003	0.048
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-			0.006	0.013	0.025	0.050	0.200
4,6-di-tert-Butyl-m-cresol					0.029	0.009	0.037
Phenol, 2,4-bis(1,1-dimethylethyl)-							0.157
Diethyl Phthalate			0.057				
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-						0.001	0.027
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-							0.028
Benzophenone			0.003	0.191		0.002	0.477
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-			0.001	0.009	0.001	0.003	0.015
Phenol, 4-(1,1-dimethylpropyl)-			0.001	0.008		0.002	0.009
4-Methyl-2-tert-octylphenol			0.002	0.010		0.003	0.012
(52.583) unknown alkyl phenol				0.008		0.002	0.011
(52.648) unknown alkyl phenol		0.001	0.002	0.010		0.002	0.012

Compound	PET.E.T1S0	PET.E.T1S1	PET.E.T2S1	PET.E.T3S1	PET.E.T1S2	PET.E.T2S2	PET.E.T3S2
Phenol, 4-(1,1,3,3-tetramethylbutyl)-			0.004	0.013	0.004	0.008	0.034
3,5-di-tert-Butyl-4-hydroxybenzaldehyde				0.005		0.006	0.078
Phenanthrene	0.038			0.022		0.001	0.111
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester			0.040		0.063	0.155	0.173
Ethanone, 2,2-dimethoxy-1,2-diphenyl-			0.001	0.015	0.001	0.002	0.097
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester			0.005	0.012	0.001	0.007	0.002
1-Methyldibenzothiophene	0.001			0.002	0.001	0.001	0.013
Dibutyl phthalate			0.205			3.071	
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione							
1-Propene-1,2,3-tricarboxylic acid, tributyl ester	0.017						
2,5-di-tert-Butyl-1,4-benzoquinone					0.016	0.040	0.022
Tributyl acetylcitrate							

Table A. 10. Storage Experiment Results for PET from Manufacture I (Commercially filled bottle so no overnight data)

Compound	No Data	PET.I.T1S1	PET.I.T2S1	No Data	PET.I.T1S2	PET.I.T2S2	PET.I.T3S2
2-Ethyl-3-methoxy-2-cyclopentenone			0.005		0.005		0.013
Benzothiazole		0.060					0.016
1,4-Dioxane-2,5-dione, 3,6-dimethyl-							
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-							
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone		0.002	0.002		0.006	0.006	0.047
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-					0.064	0.026	0.230
4,6-di-tert-Butyl-m-cresol					0.156	0.015	0.019
Phenol, 2,4-bis(1,1-dimethylethyl)-							0.045
Diethyl Phthalate							
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-					0.005		0.021
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-							0.020
Benzophenone		0.006					0.486
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-		0.003	0.003		0.007	0.003	0.015
Phenol, 4-(1,1-dimethylpropyl)-		0.003	0.006		0.010	0.008	0.010
4-Methyl-2-tert-octylphenol		0.005	0.008		0.014	0.010	0.013
(52.583) unknown alkyl phenol		0.004	0.007		0.013	0.011	0.010
(52.648) unknown alkyl phenol		0.005	0.009		0.016	0.013	0.013

Compound	No Data	PET.I.T1S1	PET.I.T2S1	No Data	PET.I.T1S2	PET.I.T2S2	PET.I.T3S2
Phenol, 4-(1,1,3,3-tetramethylbutyl)-							0.030
3,5-di-tert-Butyl-4-hydroxybenzaldehyde					0.069		0.026
Phenanthrene		0.021					0.146
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester						0.007	0.033
Ethanone, 2,2-dimethoxy-1,2-diphenyl-		0.002	0.001		0.003	0.002	0.152
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester		0.001	0.012		0.003	0.007	0.002
1-Methyldibenzothiophene					0.002	0.001	0.018
Dibutyl phthalate							
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione							
1-Propene-1,2,3-tricarboxylic acid, tributyl ester							
2,5-di-tert-Butyl-1,4-benzoquinone					0.036	0.073	0.112
Tributyl acetylcitrate			0.009				

Table A. 11. Storage Experiment Results for PLA from Manufacture F (clear plastic) – no data for highest temperature

Compound	PLA.Fc.T1S0	PLA.Fc.T1S1	PLA.Fc.T2S1	No Data	PLA.Fc.T1S2	PLA.Fc.T2S2	No Data
2-Ethyl-3-methoxy-2-cyclopentenone		0.005	0.022		0.011	0.043	
Benzothiazole		0.001				0.008	
1,4-Dioxane-2,5-dione, 3,6-dimethyl-		0.016					
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-		0.021			0.007		
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone		0.010	0.020		0.022	0.053	
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	0.023	0.032	0.040		0.220	0.568	
4,6-di-tert-Butyl-m-cresol					0.018	0.023	
Phenol, 2,4-bis(1,1-dimethylethyl)-			0.115			0.397	
Diethyl Phthalate		0.416					
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-		0.013	0.007		0.011	0.036	
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-		0.021				0.010	
Benzophenone		0.016	0.287		0.039	0.497	
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-			0.002		0.002	0.004	
Phenol, 4-(1,1-dimethylpropyl)-						0.003	
4-Methyl-2-tert-octylphenol			0.001		0.002	0.004	
(52.583) unknown alkyl phenol			0.001			0.003	
(52.648) unknown alkyl phenol			0.002		0.001	0.004	

Compound	PLA.Fc.T1S0	PLA.Fc.T1S1	PLA.Fc.T2S1	No Data	PLA.Fc.T1S2	PLA.Fc.T2S2	No Data
Phenol, 4-(1,1,3,3-tetramethylbutyl)-		0.002	0.003		0.002	0.009	
3,5-di-tert-Butyl-4-hydroxybenzaldehyde		0.016	0.069		0.006	0.174	
Phenanthrene		0.012	0.033		0.002	0.110	
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	0.040	0.155	0.136		0.226	0.482	
Ethanone, 2,2-dimethoxy-1,2-diphenyl-			0.006		0.004	0.036	
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester		0.004	0.015		0.007	0.013	
1-Methyldibenzothiophene			0.002		0.001	0.013	
Dibutyl phthalate					2.079		
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione							
1-Propene-1,2,3-tricarboxylic acid, tributyl ester	0.069	0.022	0.003		0.001		
2,5-di-tert-Butyl-1,4-benzoquinone					0.005		
Tributyl acetylcitrate					0.009	0.006	

Table A. 12. Storage Experiment Results for PLA from Manufacture F (green plastic) – no data for highest temperature

Compound	No Data ¹	PLA.Fg.T1S1	PLA.Fg.T2S1	No Data	PLA.Fg.T1S2	PLA.Fg.T2S2	No Data
2-Ethyl-3-methoxy-2-cyclopentenone		0.004	0.023		0.008	0.038	
Benzothiazole		0.098				0.006	
1,4-Dioxane-2,5-dione, 3,6-dimethyl-		1.056					
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-		0.906					
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone		0.003	0.033		0.014	0.043	
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-		0.013	0.266		0.182	0.389	
4,6-di-tert-Butyl-m-cresol		0.002	0.001		0.030	0.043	
Phenol, 2,4-bis(1,1-dimethylethyl)-			0.137			0.333	
Diethyl Phthalate		0.016	0.064				
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-			0.016		0.011	0.013	
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-							
Benzophenone		0.001	0.308		0.017	0.509	
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-			0.003			0.002	
Phenol, 4-(1,1-dimethylpropyl)-			0.001		0.001	0.002	
4-Methyl-2-tert-octylphenol			0.002			0.002	

Compound	No Data ¹	PLA.Fg.T1S1	PLA.Fg.T2S1	No Data	PLA.Fg.T1S2	PLA.Fg.T2S2	No Data
(52.583) unknown alkyl phenol			0.001			0.002	
(52.648) unknown alkyl phenol			0.002			0.003	
Phenol, 4-(1,1,3,3-tetramethylbutyl)-		0.001	0.004			0.004	
3,5-di-tert-Butyl-4-hydroxybenzaldehyde		0.010	0.090		0.025	0.177	
Phenanthrene		0.027	0.033		0.009	0.088	
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester		0.084	0.291		0.131	0.149	
Ethanone, 2,2-dimethoxy-1,2-diphenyl-		0.001	0.006		0.001	0.036	
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester		0.001	0.019		0.005	0.011	
1-Methyldibenzothiophene			0.002		0.001	0.009	
Dibutyl phthalate							
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione							
1-Propene-1,2,3-tricarboxylic acid, tributyl ester							
2,5-di-tert-Butyl-1,4-benzoquinone						0.007	
Tributyl acetylcitrate							

¹ no data available for overnight storage condition for PLA-F(green) due to sample contamination during extraction.

Table A. 13. Storage Experiment Results for PLA from Manufacture G – no data for highest temperature

Compound	PLA.G.T1S0	PLA.G.T1S1	PLA.G.T2S1	No Data	PLA.G.T1S2	PLA.G.T2S2	No Data
2-Ethyl-3-methoxy-2-cyclopentenone			0.026		0.008	0.085	
Benzothiazole							
1,4-Dioxane-2,5-dione, 3,6-dimethyl-							
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-					0.002		
2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone		0.040	0.064		0.024	0.246	
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-		0.062	0.031		0.184	0.899	
4,6-di-tert-Butyl-m-cresol		0.005			0.053	0.156	
Phenol, 2,4-bis(1,1-dimethylethyl)-			0.099			0.448	
Diethyl Phthalate							
1,1'-Biphenyl, 2,2',5,5'-tetramethyl-		0.011	0.024		0.015	0.014	
1,1'-Biphenyl, 3,3',4,4'-tetramethyl-		0.014					
Benzophenone		0.001	0.220		0.012	0.270	
Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)-		0.003	0.004		0.001	0.007	
Phenol, 4-(1,1-dimethylpropyl)-		0.002	0.003		0.001	0.005	
4-Methyl-2-tert-octylphenol		0.002	0.004		0.002	0.007	
(52.583) unknown alkyl phenol			0.003		0.001	0.004	
(52.648) unknown alkyl phenol		0.003	0.005		0.001	0.007	

Compound	PLA.G.T1S0	PLA.G.T1S1	PLA.G.T2S1	No Data	PLA.G.T1S2	PLA.G.T2S2	No Data
Phenol, 4-(1,1,3,3-tetramethylbutyl)-		0.005	0.010		0.003	0.015	
3,5-di-tert-Butyl-4-hydroxybenzaldehyde		0.016	0.061		0.054	0.334	
Phenanthrene		0.006	0.029		0.023	0.048	
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester		0.126	0.442		0.262	0.320	
Ethanone, 2,2-dimethoxy-1,2-diphenyl-	0.001	0.002	0.005		0.003	0.006	
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester			0.014		0.001	0.004	
1-Methyldibenzothiophene			0.001		0.003	0.005	
Dibutyl phthalate		2.921			0.751	0.881	
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione							
1-Propene-1,2,3-tricarboxylic acid, tributyl ester	0.038	0.018	0.003		0.012		
2,5-di-tert-Butyl-1,4-benzoquinone							
Tributyl acetylcitrate					0.020	0.005	

Appendix D: Measured Concentration (ppb) of Elements in Water During Storage Experiment for Each Bottle Type and Manufacturer

Table A. 14. Results of Elemental Analysis for PET from Manufacturer A (ppb)

Element	PET.A.T1S0	PET.A.T1S1	PET.A.T2S1	PET.A.T3S1	PET.A.T1S2	PET.A.T2S2	PET.A.T3S2
Li		0.83	0.84	0.85	0.88	0.86	0.83
Be							
B	0.57	4.40	4.54	4.66	4.57	4.68	4.54
Na		1112.00	1058.96	1134.67	1124.50	1097.18	1145.92
Mg		497.99	496.18	510.07	497.35	491.31	508.58
Al	3.49			19.21			3.43
Si		222.49	237.37	306.70	280.97	249.50	303.58
K		232.26	213.62	220.56	259.36	262.07	241.53
Ca	70.87	1455.13	1301.92	1288.89	1678.35	1656.05	1465.28
V							
Cr							
Mn	2.43	0.41	2.60	2.34	3.36	3.79	2.41
Fe	74.54		25.91	26.61	35.44	40.71	26.39
Se	0.60	0.69	0.72	0.69	0.70	0.72	0.68
Ti							
Ni	0.70		0.20	0.20	0.29	0.31	0.18
Co	0.02		0.04	0.04	0.02	0.04	0.05
Cu	12.33	2.21	4.94	4.39	6.08	8.02	4.66
Zn	2.63		0.01		0.23	0.15	

Element	PET.A.T1S0	PET.A.T1S1	PET.A.T2S1	PET.A.T3S1	PET.A.T1S2	PET.A.T2S2	PET.A.T3S2
As				0.02		0.01	0.02
Rb	0.13	0.14	0.14	0.15	0.16	0.15	0.15
Sr	1.15	16.96	16.93	17.42	17.87	17.71	17.87
P							
Mo	0.07	0.10	0.09	0.09	0.07	0.07	0.08
Ag							
Cd							
Sb	0.09	0.29	0.36	1.20	0.28	0.41	1.48
Cs							
Ba	7.07	4.27	3.77	4.29	3.79	3.97	3.78
Ce							
Eu							
Pb	0.67		0.09	0.11	0.16	0.18	0.08
Bi							
Th							
U							
Sn							

Table A. 15. Results of Elemental Analysis for PET from Manufacturer C (ppb)

Element	PET.C.T1S0	PET.C.T1S1	PET.C.T2S1	PET.C.T3S1	PET.C.T1S2	PET.C.T2S2	PET.C.T3S2
Li		0.85	0.82	0.82	0.84	0.84	0.83
Be							
B	0.94	4.85	4.79	4.88	5.08	5.00	4.92
Na		1110.23	1107.82	1063.18	702.92	852.91	877.42
Mg		503.36	496.26	486.64	458.68	468.37	484.75
Al	3.60			6.46			4.32
Si		207.07	197.09	186.37	180.35	235.73	256.51
K	1.67	266.53	261.42	246.34	278.19	277.63	269.87
Ca	270.60	1703.44	1718.32	1525.54	1829.46	1855.43	1599.32
V							
Cr							
Mn	2.84	2.27	2.56	2.27	2.23	2.51	2.24
Fe	73.73	18.31	29.70	27.54	26.71	30.33	25.81
Se	0.53	0.67	0.68	0.64	0.73	0.73	0.64
Ti							
Ni	0.63	0.11	0.19	0.19	0.19	0.21	0.19
Co	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cu	12.21	3.64	5.34	4.46	4.41	5.37	4.41
Zn	3.52					0.03	0.05
As				0.01	0.01	0.01	0.01
Rb	0.13	0.13	0.13	0.14	0.14	0.15	0.14
Sr	0.78	17.52	17.30	18.03	18.43	18.80	19.00
P							
Mo		0.07	0.07	0.07	0.08	0.08	0.08
Ag							
Cd							

Element	PET.C.T1S0	PET.C.T1S1	PET.C.T2S1	PET.C.T3S1	PET.C.T1S2	PET.C.T2S2	PET.C.T3S2
Sb	0.23	0.71	1.48	4.44	0.82	1.93	5.93
Cs							
Ba	7.47	3.71	4.74	3.48	3.49	3.62	3.57
Ce							
Eu							
Pb	0.66		0.10	0.08	0.11	0.15	0.08
Bi							
Th							
U							
Sn							

Table A. 16. Results of Elemental Analysis for PET from Manufacturer E (ppb)

Element	PET.E.T1S0	PET.E.T1S1	PET.E.T2S1	PET.E.T3S1	PET.E.T1S2	PET.E.T2S2	PET.E.T3S2
Li		1.09	1.07	1.07	1.09	1.08	1.14
Be							
B	1.52	6.85	6.80	6.91	6.60	6.74	6.56
Na		402.75	415.98	428.52	481.41	518.19	573.12
Mg		331.55	333.52	343.92	354.39	369.44	383.91
Al	3.91						
Si							
K	5.99	203.64	193.83	171.60	212.62	199.59	182.13
Ca		134.98	134.05		226.15	180.05	
V							
Cr		0.01				0.01	
Mn	1.38	2.32	2.42	2.30	2.41	2.41	2.25
Fe	62.86	23.15	29.93	43.17	28.00	30.11	35.90
Se	0.60	0.65	0.76	0.59	0.68	0.70	0.51
Ti							
Ni	0.47		0.01	0.09	0.01	0.02	0.06
Co	0.01	0.02	0.02	0.03	0.02	0.02	0.03
Cu	11.32	4.28	4.52	5.53	4.19	4.61	5.10
Zn	3.62	1.28	0.87	0.85	1.12	0.85	0.49
As		0.09	0.08	0.10	0.10	0.09	0.11
Rb	0.15	0.15	0.14	0.15	0.15	0.15	0.16
Sr	37.22	107.33	108.59	109.14	108.83	108.72	109.59
P		2.37		6.75	8.07	0.84	15.20
Mo		0.12	0.10	0.09	0.09	0.08	0.08
Ag							
Cd							

Element	PET.E.T1S0	PET.E.T1S1	PET.E.T2S1	PET.E.T3S1	PET.E.T1S2	PET.E.T2S2	PET.E.T3S2
Sb	0.18	0.35	0.66	2.33	0.39	0.69	2.67
Cs							
Ba	7.44	3.71	3.94	3.48	3.40	3.49	3.82
Ce	0.01						
Eu							
Pb	0.44		0.08	0.26	0.06	0.07	0.16
Bi							
Th							
U							
Sn							

Table A. 17. Results of Elemental Analysis for PET from Manufacturer I (ppb)

Element	No Data	PET.I.T1S1	PET.I.T2S1	PET.I.T3S1	PET.I.T1S2	PET.I.T2S2	PET.I.T3S2
Li		0.15	0.17	0.19	0.15	0.16	0.17
Be							
B		27.67	27.20	27.58	25.45	23.22	23.64
Na		1132.52	1127.69	1175.28	1229.69	1272.53	1274.56
Mg		491.64	491.25	511.91	528.47	532.13	534.35
Al		2.07	1.70	1.96	1.85	1.50	1.13
Si		3655.74	3633.17	3707.88	3859.44	3885.63	3907.14
K		380.60	379.70	402.02	382.35	366.27	368.95
Ca		1405.84	1411.76	1431.51	1499.89	1560.18	1529.12
V		0.61	0.60	0.63	0.60	0.55	0.56
Cr		0.17	0.18	0.18	0.17	0.15	0.16
Mn		0.03		0.04	0.01	0.05	0.02
Fe							
Se					0.61	0.60	0.58
Ti		1.47	0.85	0.84	0.84	0.98	0.71
Ni		0.05	0.04	0.06	0.05		
Co		0.01		0.01			
Cu		0.04	0.02	0.07	0.06		
Zn		1.05	1.30	5.02	0.98	1.28	0.70
As		0.09	0.08	0.08	0.10	0.08	0.08
Rb		0.93	0.93	0.97	0.94	0.91	0.93
Sr		48.31	48.10	49.79	33.68	17.87	17.92
P		72.72	72.83	81.91	64.55	51.77	54.61
Mo		0.03	0.03	0.03	0.09	0.06	0.04
Ag							
Cd							

Element	No Data	PET.I.T1S1	PET.I.T2S1	PET.I.T3S1	PET.I.T1S2	PET.I.T2S2	PET.I.T3S2
Sb		0.02	0.03	0.05	0.03	0.03	0.05
Cs		0.01	0.01	0.01	0.01	0.01	0.01
Ba		4.04	4.83	4.95	4.05	3.97	3.97
Ce		0.01			0.02		
Eu							
Pb							
Bi							
Th							
U							
Sn							

Table A. 18. Results of Elemental Analysis for PLA from Manufacturer F (clear) (ppb)

Element	PLA.Fc.T1S0	PLA.Fc.T1S1	PLA.Fc.T2S1	No Data	PLA.Fc.T1S2	PLA.Fc.T2S2	No Data
Li		0.92	0.87		1.00	0.88	
Be							
B	0.21	4.96	4.90		5.46	5.21	
Na	87.55	1780.82	1646.71		2042.05	1836.43	
Mg		605.36	580.00		678.53	592.97	
Al	3.49						
Si		433.25	359.48		663.23	376.22	
K		209.21	197.04		251.16	216.81	
Ca		1273.55	1169.80		1628.75	1418.06	
V							
Cr					0.01		
Mn	2.53	0.92	0.63		0.87	1.00	
Fe	75.72	16.15	13.53		19.82	19.38	
Se	0.51	0.66	0.65		0.72	0.68	
Ti							
Ni	0.80	0.08	0.06		0.14	0.13	
Co		0.01			0.01	0.01	
Cu	12.73	4.06	3.06		3.86	4.27	
Zn	2.62	0.05			0.14		
As		0.05	0.06		0.10	0.05	
Rb	0.14	0.17	0.16		0.22	0.17	
Sr		18.81	18.30		22.14	19.34	
P							
Mo		0.09	0.09		0.11	0.09	
Ag							
Cd							

Element	PLA.Fc.T1S0	PLA.Fc.T1S1	PLA.Fc.T2S1	No Data	PLA.Fc.T1S2	PLA.Fc.T2S2	No Data
Sb	0.01	0.01	0.01		0.01	0.01	
Cs							
Ba	7.95	3.53	3.46		3.81	2.95	
Ce							
Eu							
Pb	0.78	0.05	0.08		0.21	0.10	
Bi							
Th							
U							
Sn			0.02		0.03	0.05	

Table A. 19. Results of Elemental Analysis for PLA from Manufacturer F (green) (ppb)

Element	No Data	PLA.Fg.T1S1	PLA.Fg.T2S1	No Data	PLA.Fg.T1S2	PLA.Fg.T2S2	No Data
Li		0.88	0.85		0.95	0.85	
Be							
B		4.29	5.36		5.64	5.10	
Na		1757.45	1570.41		1881.67	1534.29	
Mg		599.58	561.67		641.14	565.70	
Al							
Si		357.59	297.35		572.94	354.36	
K		230.31	209.59		260.18	220.16	
Ca		1446.71	1335.14		1715.32	1401.78	
V							
Cr							
Mn		0.04	1.05		0.95	0.77	
Fe		3.61	19.45		19.10	16.08	
Se		0.68	0.65		0.71	0.67	
Ti			0.20				
Ni		0.02	0.13		0.15	0.10	
Co			0.01		0.01	0.01	
Cu		1.54	4.34		4.00	3.33	
Zn			0.23		0.18		
As		0.05	0.05		0.08	0.07	
Rb		0.17	0.17		0.20	0.15	
Sr		19.76	19.34		22.08	19.43	
P							
Mo		0.08	0.08		0.09	0.08	
Ag							
Cd							

Element	No Data	PLA.Fg.T1S1	PLA.Fg.T2S1	No Data	PLA.Fg.T1S2	PLA.Fg.T2S2	No Data
Sb		0.01	0.01		0.01	0.01	
Cs							
Ba		3.31	3.52		3.65	3.00	
Ce							
Eu							
Pb			0.16		0.18	0.13	
Bi							
Th							
U							
Sn		0.07			0.02	0.05	

Table A. 20. Results of Elemental Analysis for PLA from Manufacturer G (ppb)

Element	PLA.G.T1S0	PLA.G.T1S1	PLA.G.T2S1	No Data	PLA.G.T1S2	PLA.G.T2S2	No Data
Li		1.27	0.94		1.08	0.97	
Be							
B	1.17	6.15	4.47		5.10	4.49	
Na		1246.22	1549.84		1773.32	1493.23	
Mg		564.77	562.08		626.92	564.72	
Al	4.31						
Si		279.41	155.48		353.55	203.06	
K		266.89	203.38		241.77	214.58	
Ca		677.58	725.01		1090.03	738.59	
V							
Cr							
Mn	1.21	0.76	0.53		0.70	0.66	
Fe	75.17	6.90	13.36		14.17	15.90	
Se	0.34	0.25	0.46		0.52	0.47	
Ti		0.26					
Ni	0.76				0.01	0.01	
Co			0.01		0.01		
Cu	12.81	2.74	2.10		3.10	2.43	
Zn	3.38	0.49	0.04		0.25		
As		0.14	0.08		0.10	0.08	
Rb	0.13	0.20	0.14		0.19	0.15	
Sr	36.68	118.27	63.91		69.28	64.51	
P							
Mo		0.11	0.09		0.11	0.09	
Ag							
Cd							

Element	PLA.G.T1S0	PLA.G.T1S1	PLA.G.T2S1	No Data	PLA.G.T1S2	PLA.G.T2S2	No Data
Sb	0.03						
Cs							
Ba	8.59	3.43	3.54		3.01	2.59	
Ce							
Eu							
Pb	0.63		0.02		0.04	0.06	
Bi							
Th							
U							
Sn					0.01	0.01	

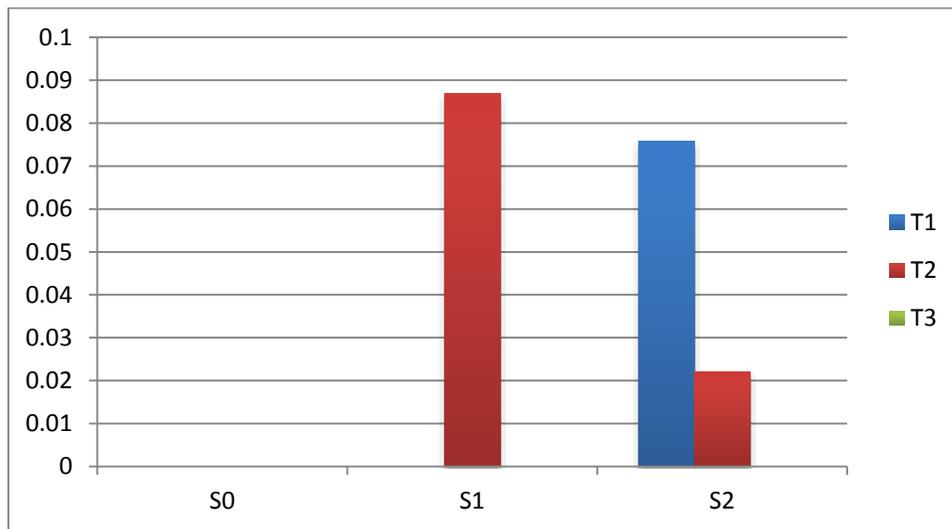
Appendix E: Graphical assessment concentration trends related to storage time and temperature for target compounds included in exposure assessment

Abbreviations:

- S0 12 hours storage
- S4W four weeks storage
- S1 Three months storage
- S2 Six months storage
- T1 ambient temperature (ca. 20 °C)
- T2 35 °C
- T3 50 °C

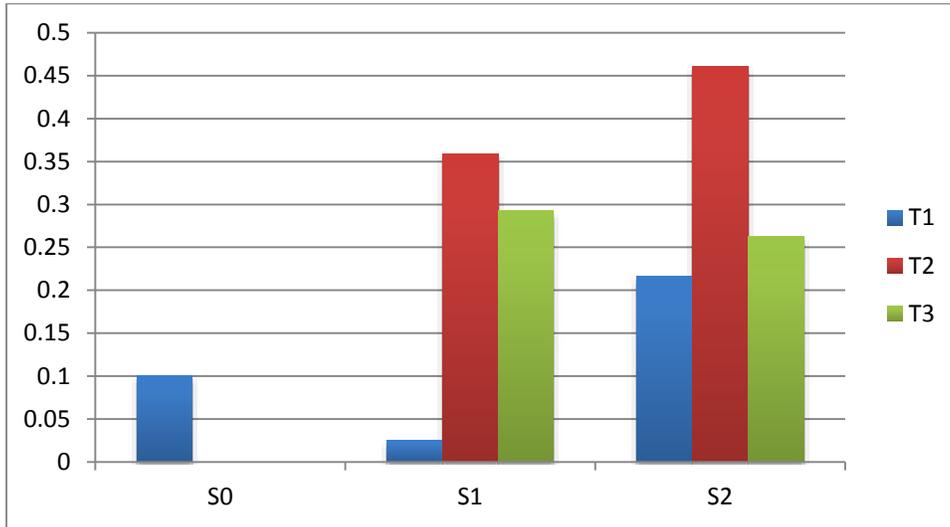
Diethyl phthalate

Diethyl phthalate (ppb) in water stored in PET-A

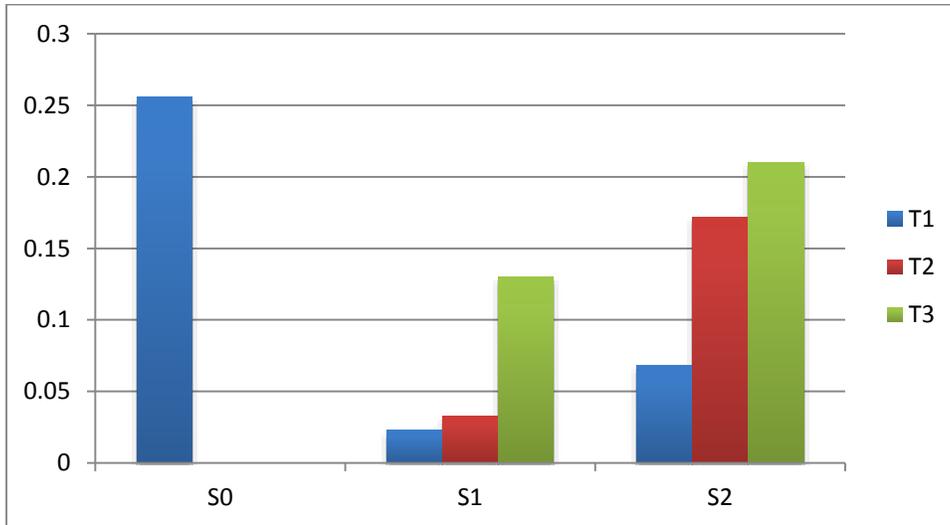


Diisobutyl phthalate

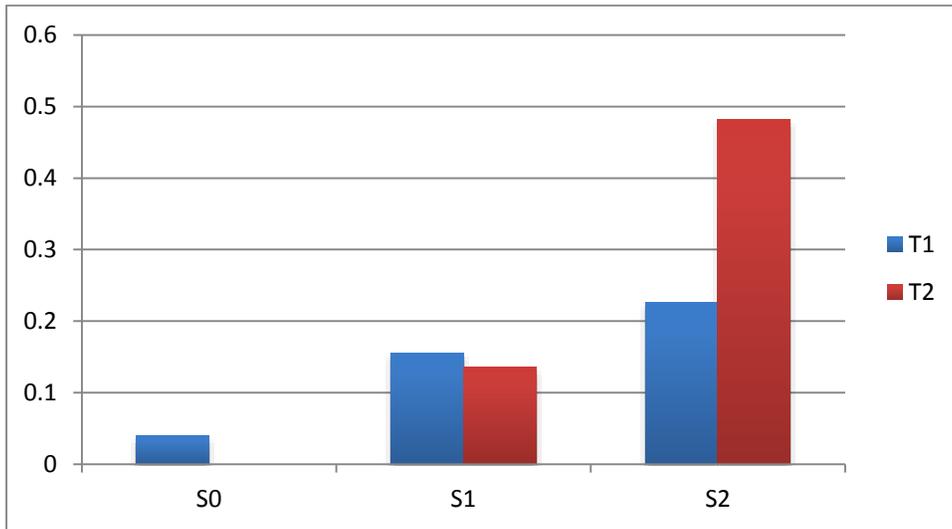
Diisobutyl phthalate (ppb) in water stored in PET-A



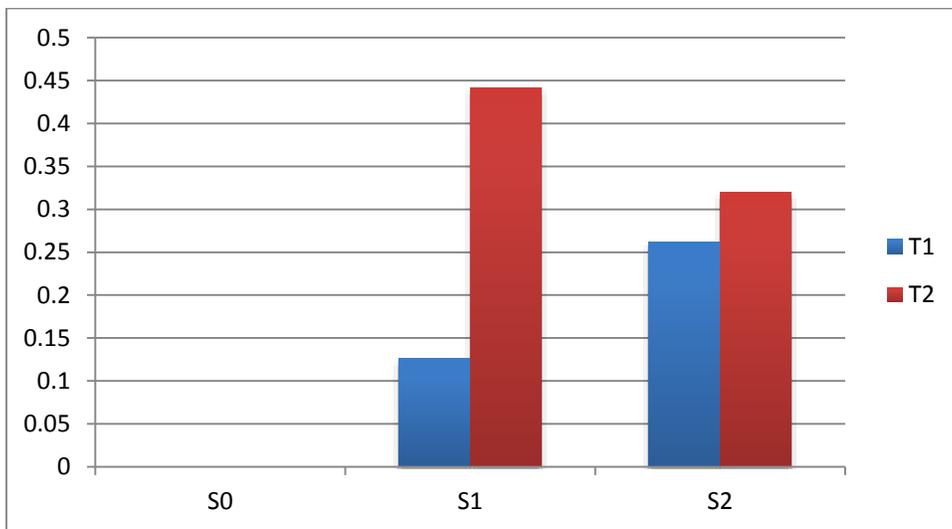
Diisobutyl phthalate (ppb) in water stored in PET-C



Diisobutyl phthalate (ppb) in water stored in PLA-Fc

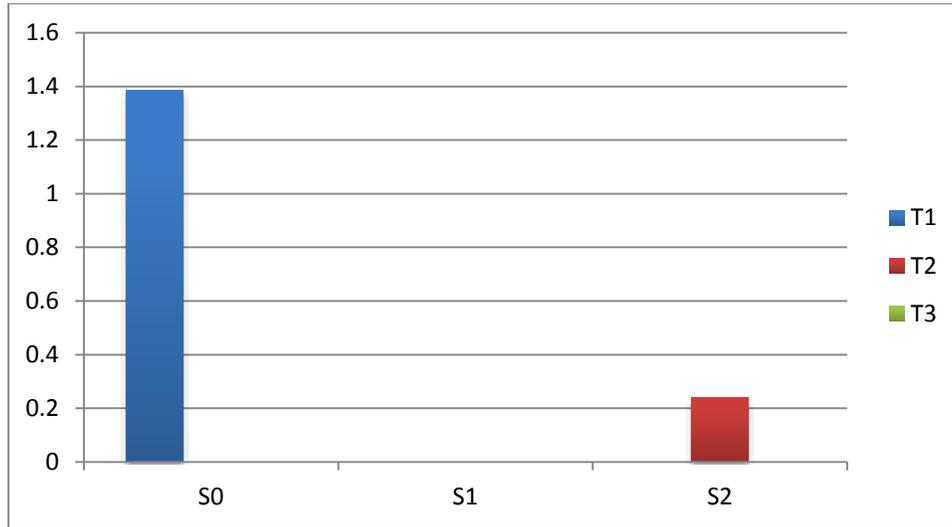


Diisobutyl phthalate (ppb) in water stored in PLA-G

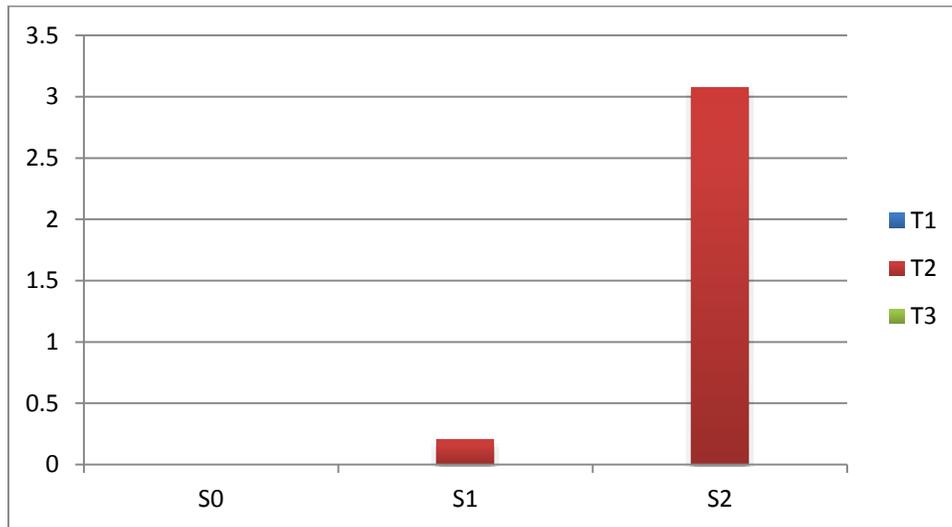


Dibutyl phthalate

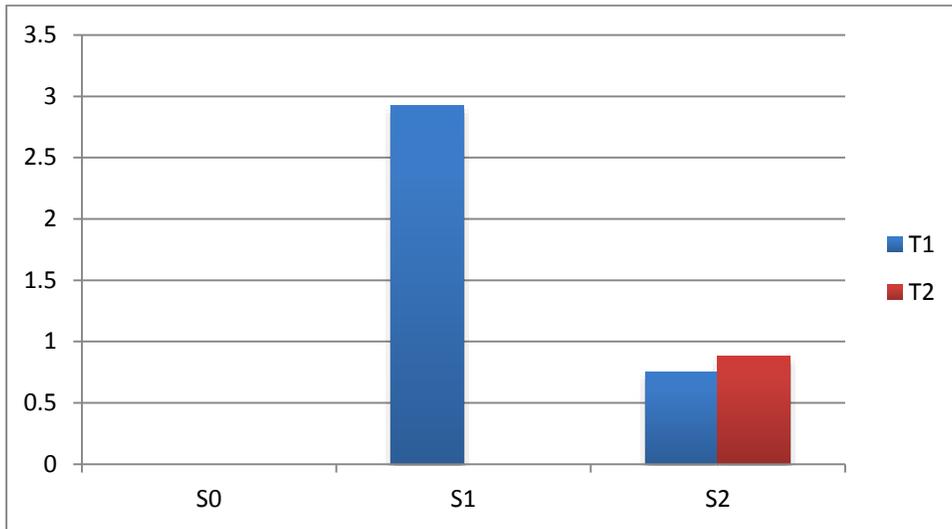
Dibutyl phthalate (ppb) in water stored in PET-C



Dibutyl phthalate (ppb) in water stored in PET-E

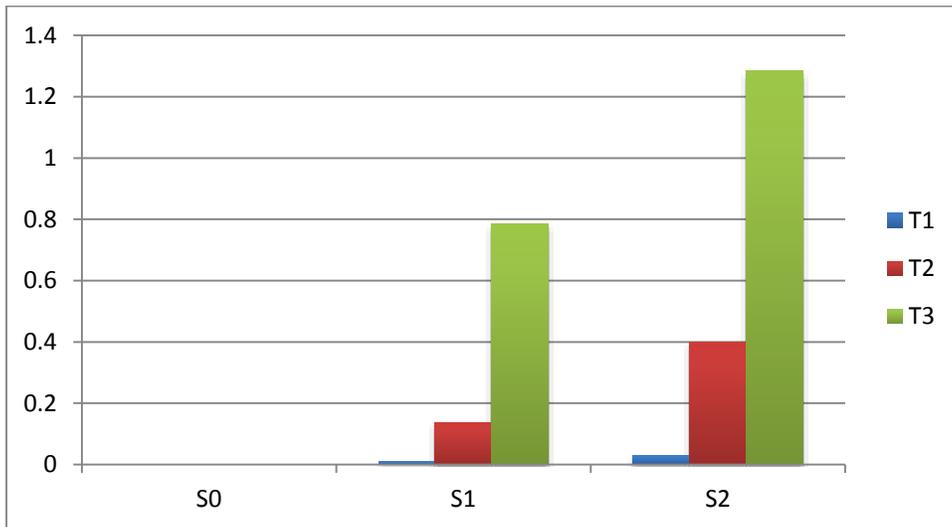


Dibutyl phthalate (ppb) in water stored in PLA-G

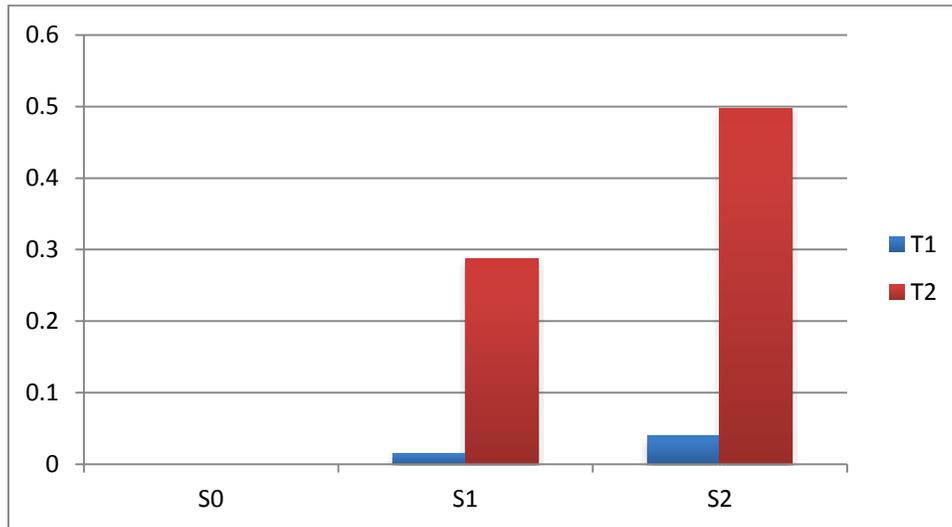


Benzophenone

Benzophenone (ppb) in water stored in PET-A

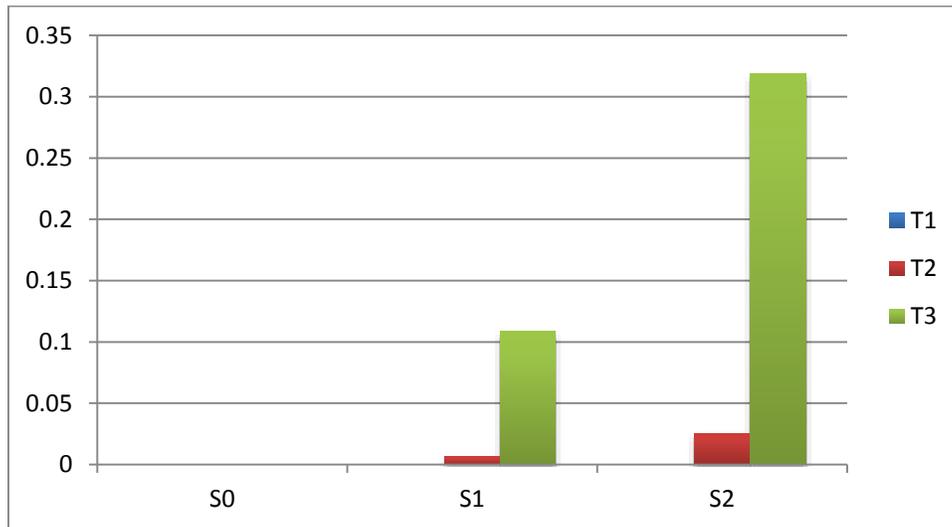


Benzophenone (ppb) in water stored in PLA-Fc

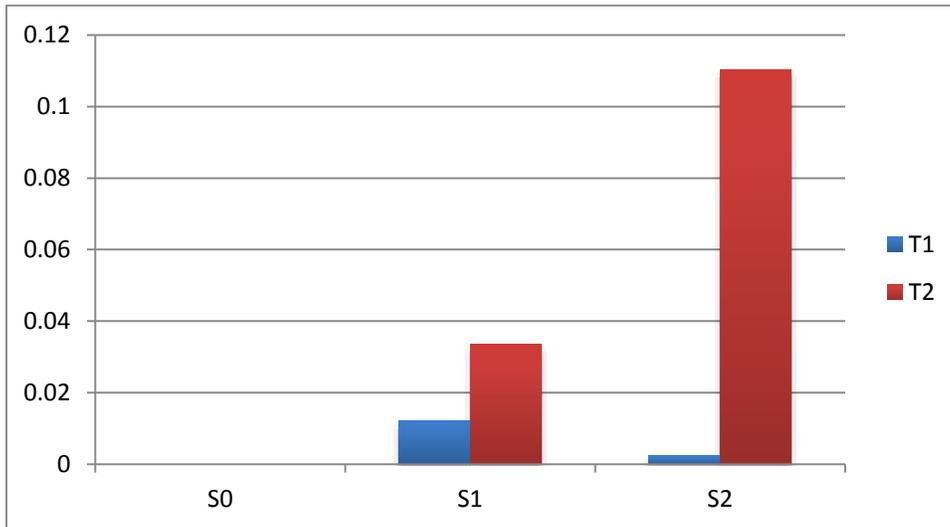


Phenanthrene

Phenanthrene (ppb) in water stored in PET-A

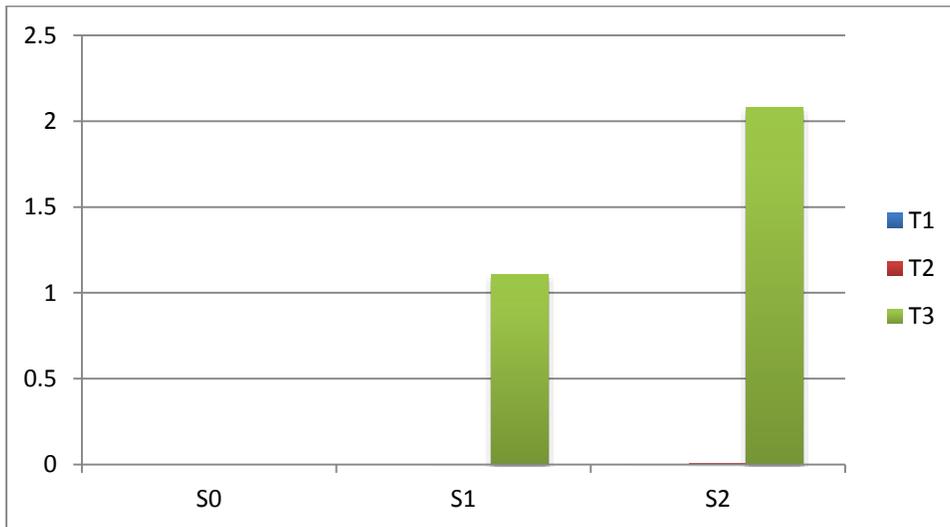


Phenanthrene (ppb) in water stored in PLA-Fc

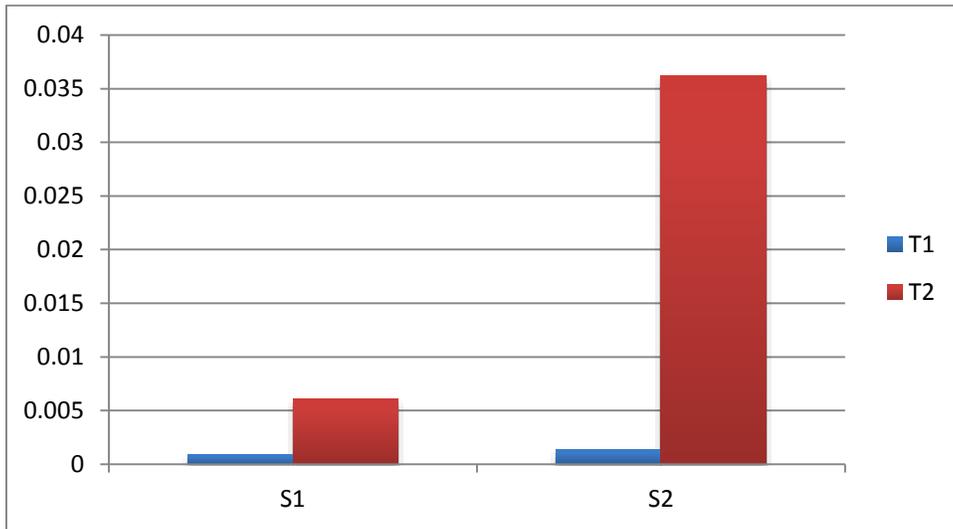


2,2-Dimethoxy-1,2-diphenylethane

2,2-Dimethoxy-1,2-diphenylethane (ppb) in water stored in PET-A

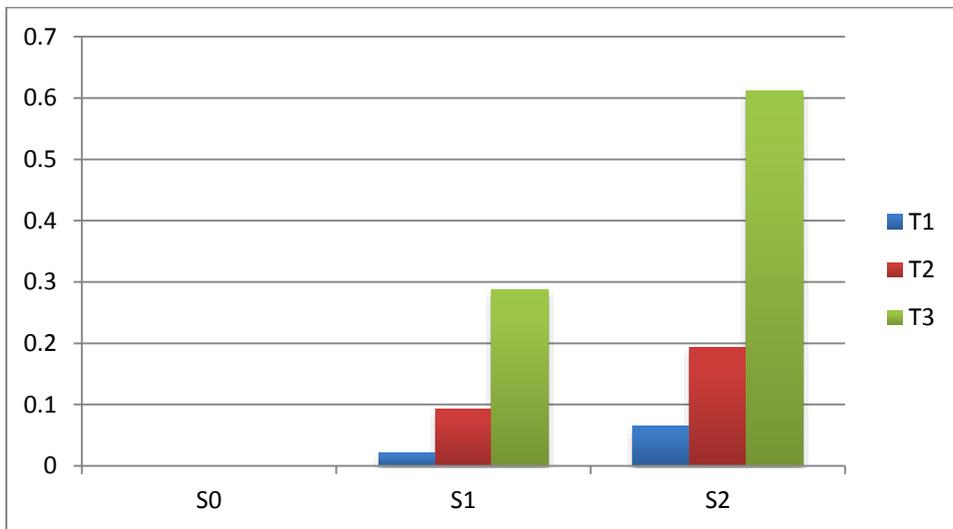


2,2-Dimethoxy-1,2-diphenylethane (ppb) in water stored in PLA-Fg

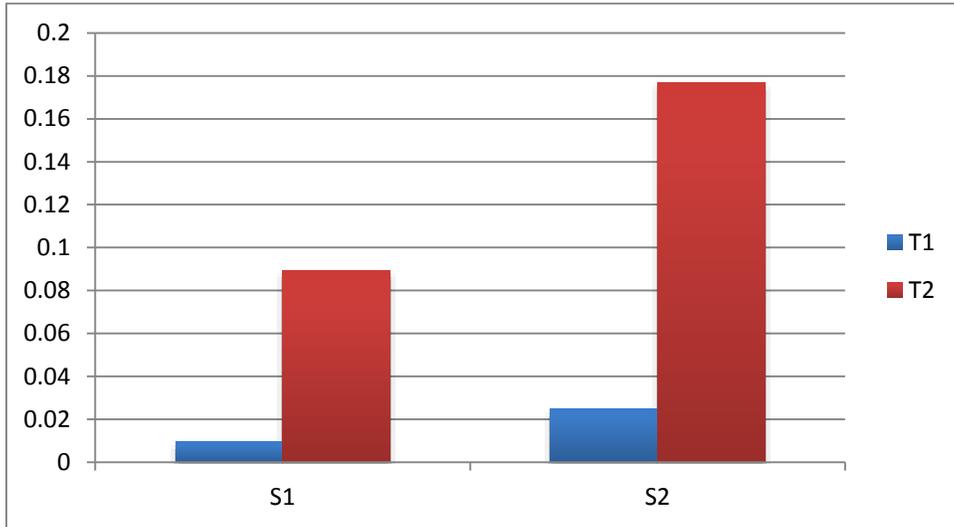


3,5-Di-tert-butyl-4-hydroxybenzaldehyde

3,5-Di-tert-butyl-4-hydroxybenzaldehyde (ppb) in water stored in PET-A

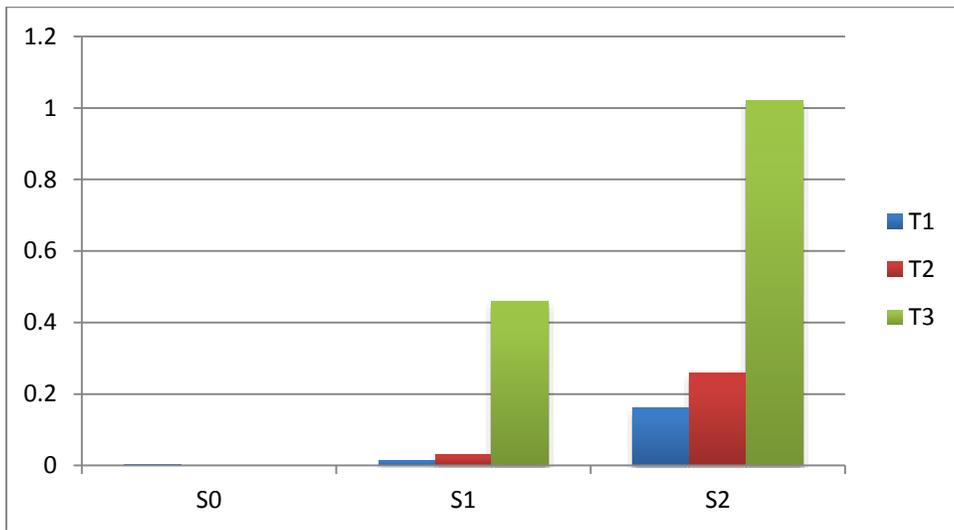


3,5-Di-tert-butyl-4-hydroxybenzaldehyde (ppb) in water stored in PLA-Fg

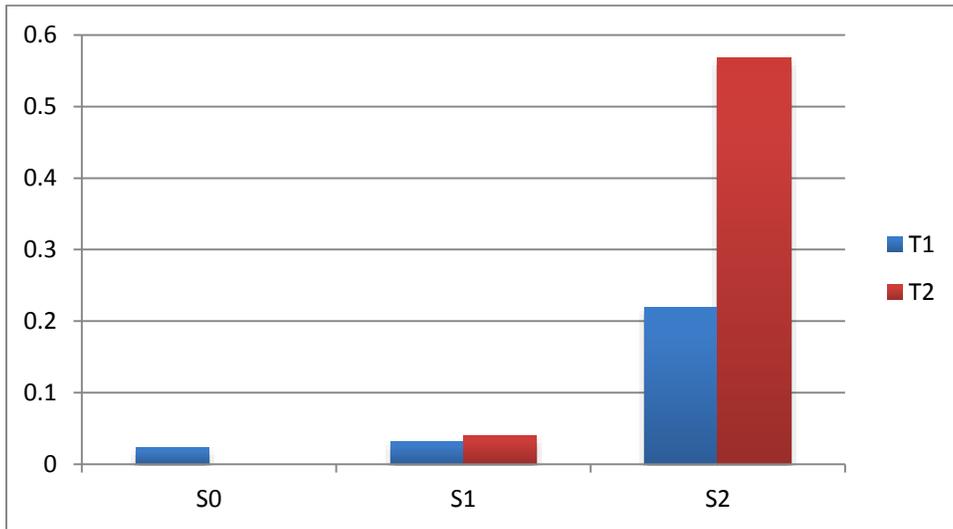


3,5-Di-tert-butylbenzoquinone

3,5-Di-tert-butylbenzoquinone (ppb) in water stored in PET-A

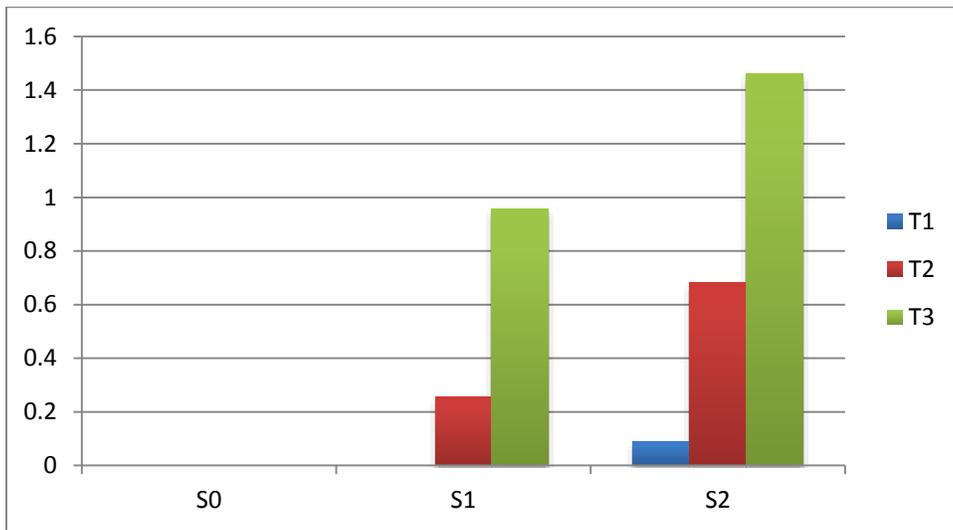


3,5-Di-tert-butylbenzoquinone (ppb) in water stored in PLA-Fc

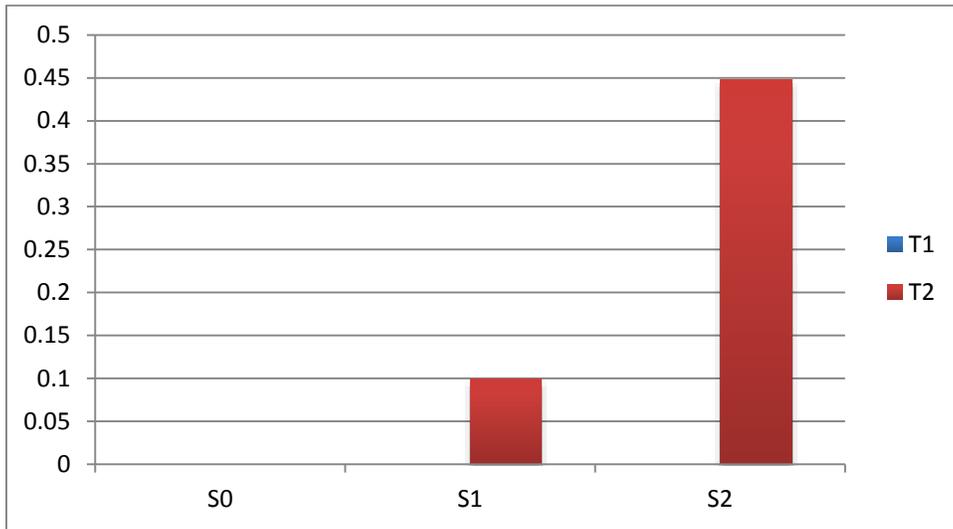


2,4-Di-tert-butylphenol

2,4-Di-tert-butylphenol (ppb) in water stored in PET-A

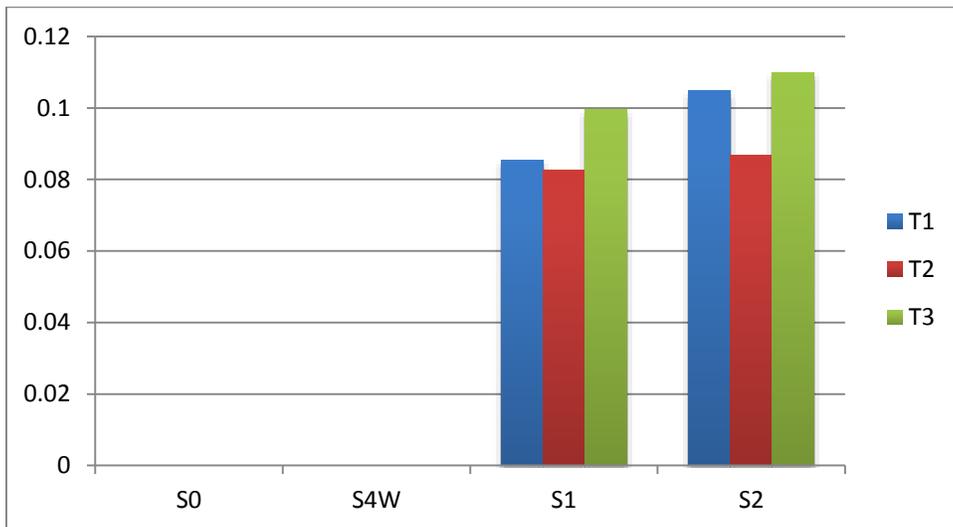


2,4-Di-tert-butylphenol (ppb) in water stored in PLA-G

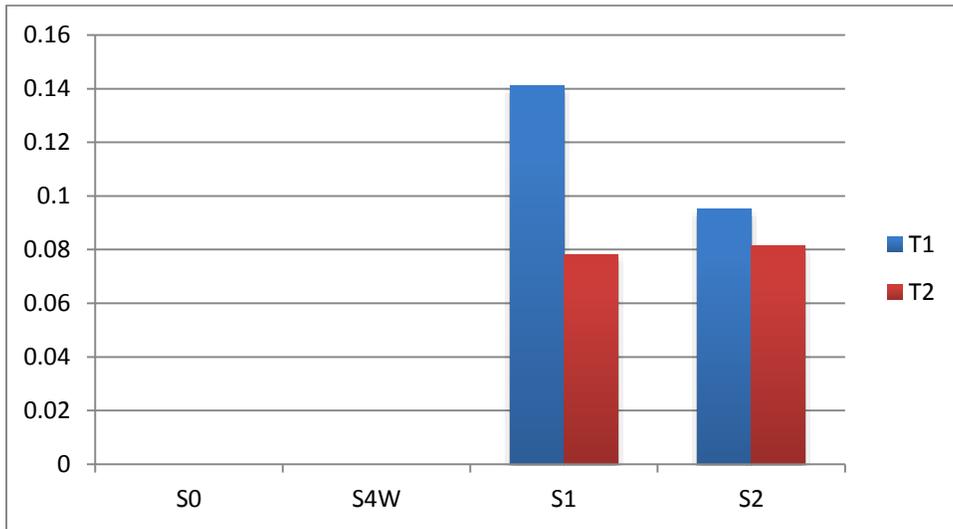


Arsenic (As)

Arsenic (ppb) in water stored in PET-E

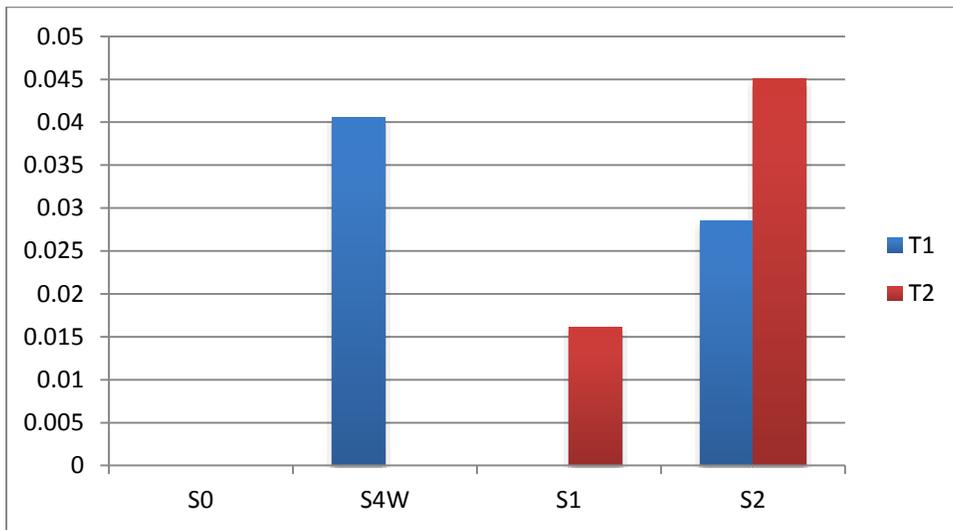


Arsenic (ppb) in water stored in PLA-G

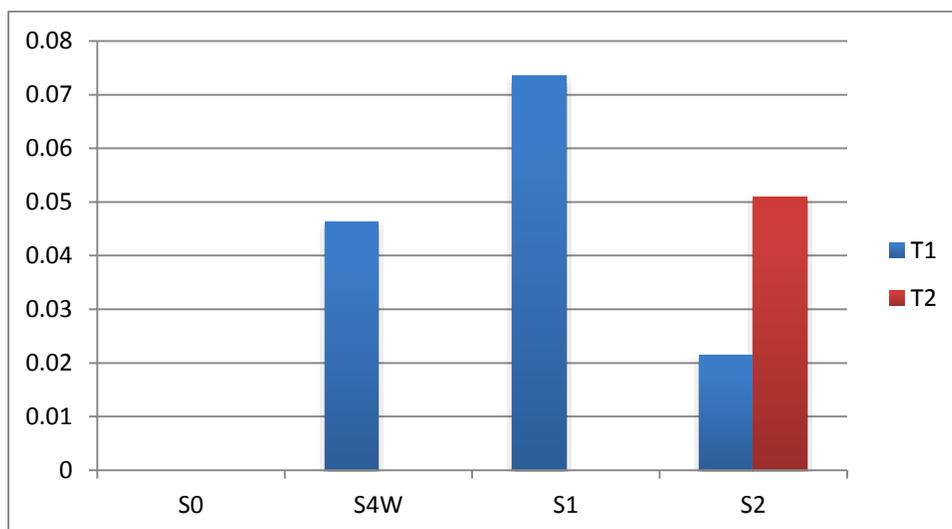


Tin (Sn)

Tin (ppb) in water stored in PLA-Fc

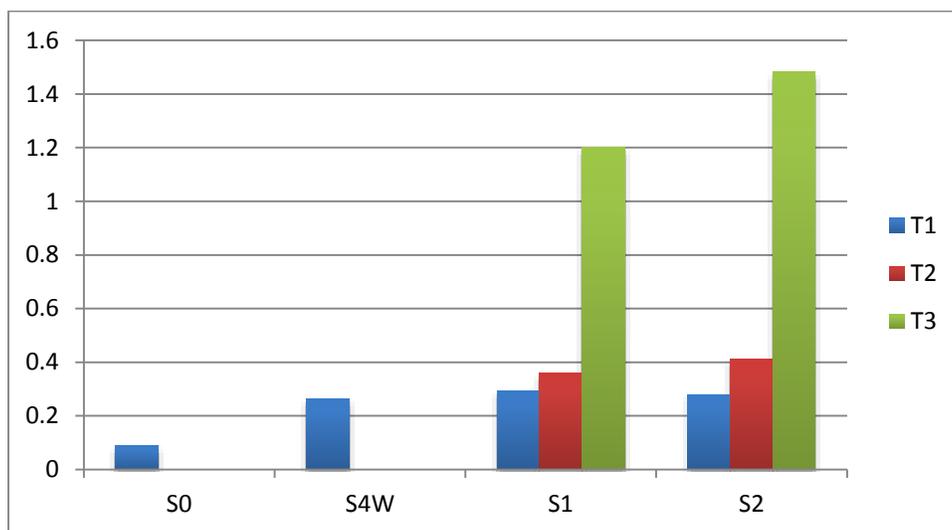


Tin (ppb) in water stored in PLA-Fg

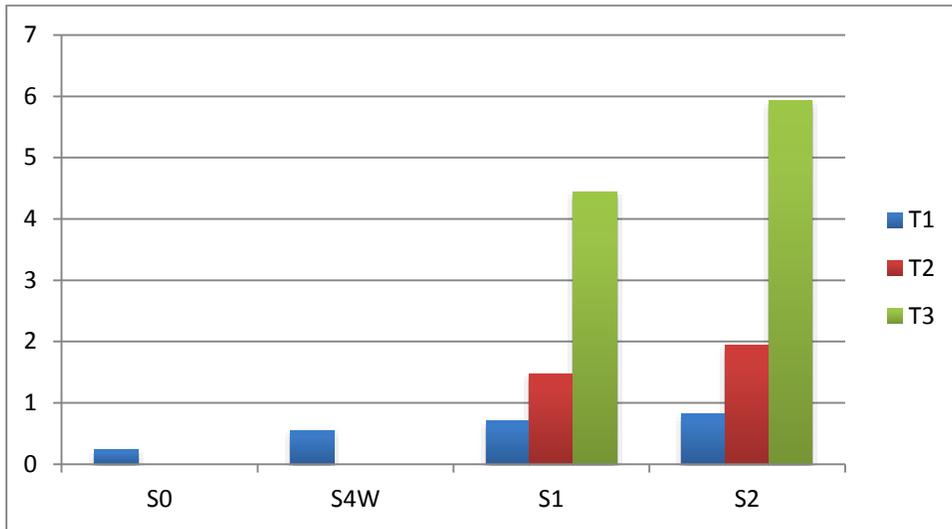


Antimony (Sb)

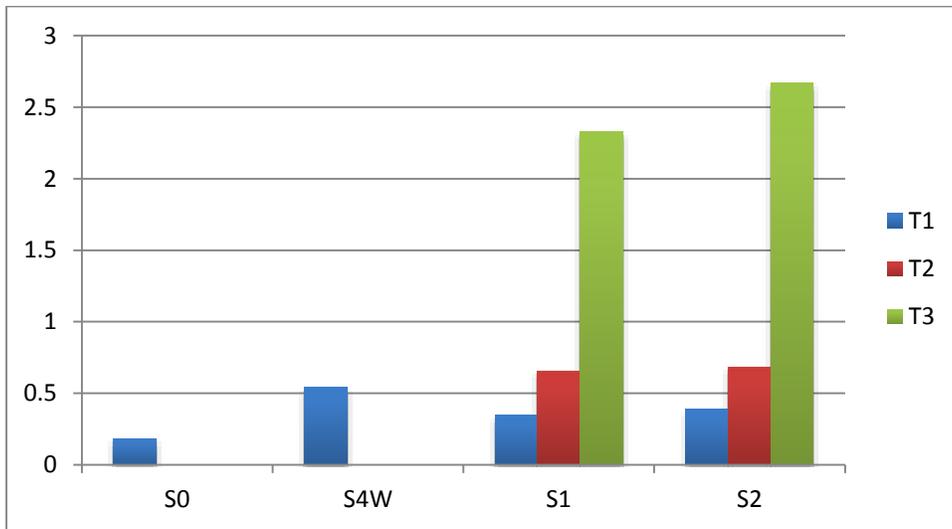
Antimony (ppb) in water stored in PET-A



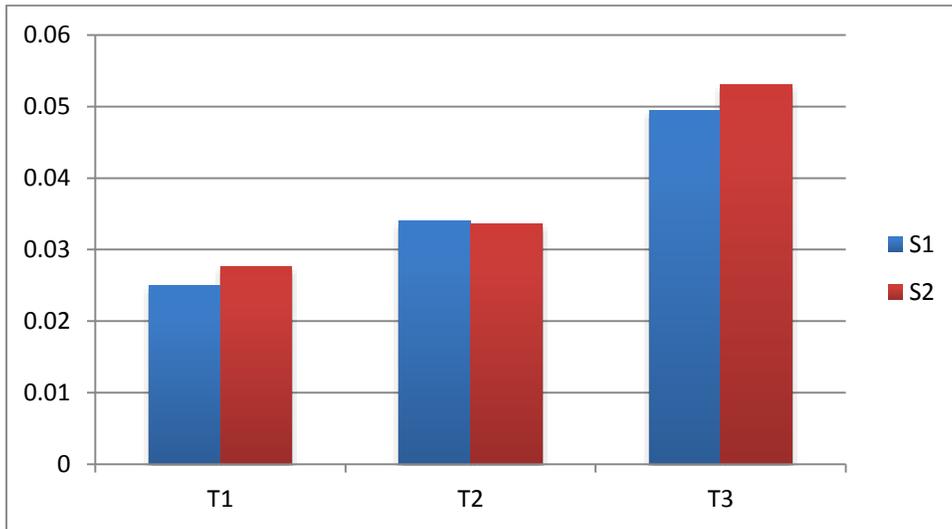
Antimony (ppb) in water stored in PET-C



Antimony (ppb) in water stored in PET-E

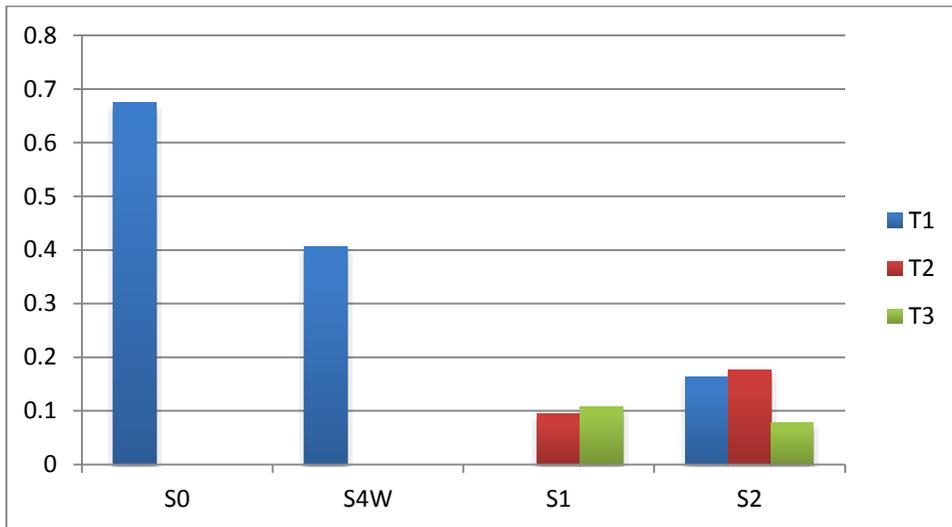


Antimony (ppb) in water stored in PET-I

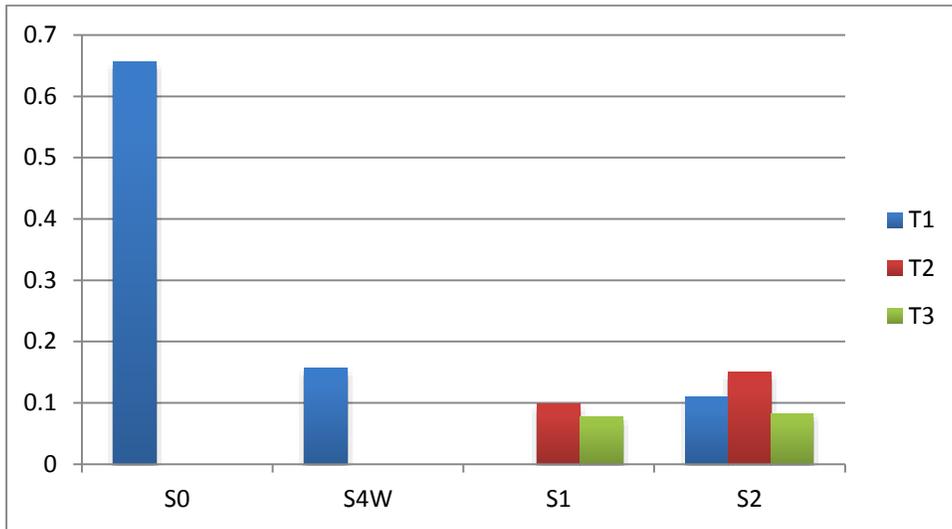


Lead (Pb)

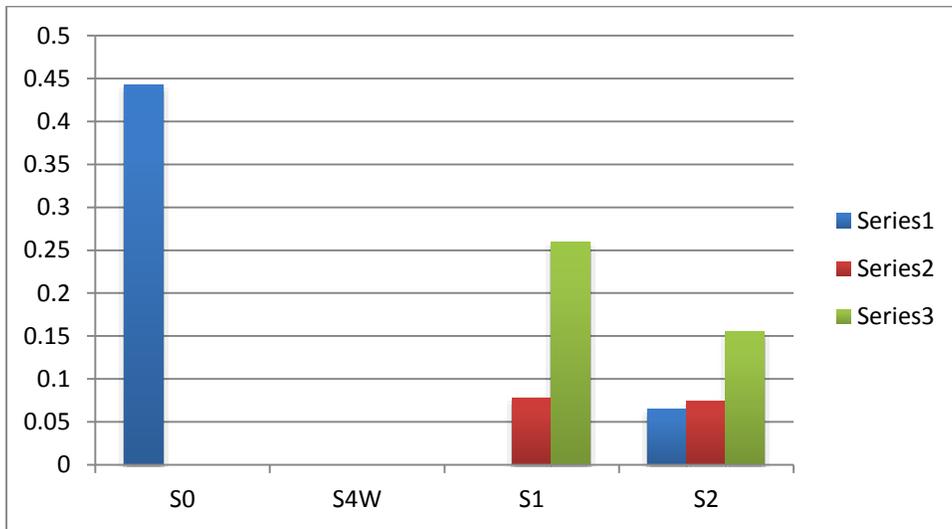
Lead (ppb) in water stored in PET-A



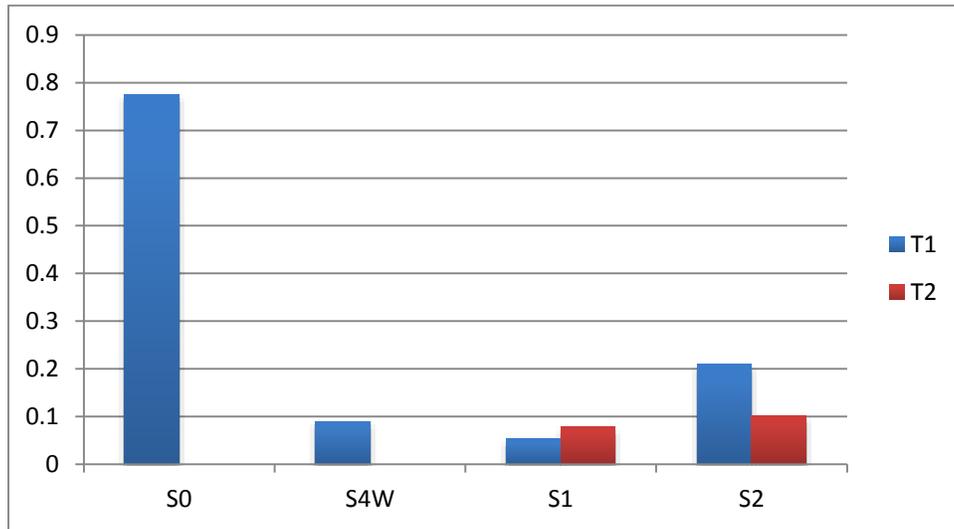
Lead (ppb) in water stored in PET-C



Lead (ppb) in water stored in PET-E



Lead (ppb) in water stored in PLA-Fc



Appendix F

Health hazard data review

We performed a review of known health effects for each of the prioritized chemicals (seven organic compounds and two elements) determined to be leaching from the plastics. Results are as follows:

Antimony (Sb)

- Mutagenic, as determined by its occurrence on the German List of Substances (Deutsche Forschungsgemeinschaft - Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area) as Group 2: “Substances that are considered to be carcinogenic for humans because sufficient data from long-term animal studies or limited evidence from animal studies substantiated by evidence from epidemiological studies indicate that they can contribute to cancer risk.” DFG (2007b) Antimony and its inorganic compounds (inhalable fraction). In: Deutsche Forschungsgemeinschaft (ed) The MAK collection for occupational health and safety. Part I: MAK value documentations, Vol 23. Wiley-VCH, Weinheim, pp 1–73.
- Induces the formation of reactive oxygen and nitrogen species in vivo and in vitro in mammalian cells. Reactive species in biological systems can alter macromolecules and membranes leading to toxicity.

Tin (Sn)

- In its inorganic form, metallic tin is generally considered to have low toxicity when ingested because of its poor absorption and rapid excretion.
- Multiple organotin compounds exhibit significant and varied toxicity, but these were not present in the bottled water.

Diisobutyl phthalate (DIBP)

- Meets the criteria for classification as toxic to reproduction in accordance with Article 57 (c) of REACH, and therefore occurs on the Candidate List for Substances of Very High Concern. ECHA Support Document for Identification of Diisobutyl Phthalate as a Substance of Very High Concern because of its carcinogenic, mutagenic or reproductive toxicity (CMR) Properties. Adopted 27 November, 2009. <http://echa.europa.eu/documents/10162/d418f8b0-ba93-402a-97fd-1e340d22c541>
- Changes in fetal testicular testosterone production are thought to be the most sensitive endpoint for DIBP effects on male reproductive development, with a NOAEL of 100 mg/kg bw/d (ECHA Support Document).
- Human evidence supports the finding in animals that prenatal phthalate exposure at environmental levels affects male reproductive development (Swan et.al, 2005)
- EC Priority Endocrine Disruptors Category 2: In vitro evidence of biological activity related to endocrine disruption

- U.S. EPA PPT Chemical Action Plan published December 30, 2009.

3,5-Di-tert-butyl-4-hydroxybenzaldehyde

- No toxicity data.

3,5-Di-tert-butylbenzoquinone

- LD₅₀ (mouse, intraperitoneal) found to be 2270 mg/kg (Kenji et.al, 1980).
- Causes oxidative DNA damage in cultured cells and DNA cleavage, via generation of reactive oxygen species (Oikawa et.al, 1998; Nagai et.al, 1993).
- Quinones are associated with chronic neurotoxic effects include vision disturbances. (O'Donoghue, 1995, p. 129).

2,4-Di-tert-butylphenol

- Previously observed to migrate into water from polyolefin bottles at room temperature, reaching concentrations up to 25 µg/L. Authors concluded no risk to human health. Skjevraak I, Brede C, Steffensen IL, Mikalsen A, Alexander J, Fjeldal P, Herikstad H. Non-targeted multi-component analytical surveillance of plastic food contact materials: Identification of substances not included in EU positive lists and their risk assessment. *Food Addit Contam.* 2005; 22(10):1012-22.
- Human estrogen receptor (hER α) activity. Creusot N, Budzinski H, Balaguer P, et. al. Effect-directed analysis of endocrine-disrupting compounds in multi-contaminated sediment: identification of novel ligands of estrogen and pregnane X receptors. *Anal Bioanal Chem.* 2013; 405(8):2553-66. doi: 10.1007/s00216-013-6708-5.
- Cytotoxicity and formation of radical oxygen species. Saito M, Atsumi T, Satoh K, Ishihara M, Iwakura I, Sakagami H, Yokoe I, Fujisawa S. Radical production and cytotoxic activity of tert-butyl-substituted phenols. *In Vitro Mol Toxicol.* 2001; 14(1):53-63.
- Cytotoxicity against human cancer cells. Malek SN, Shin SK, Wahab NA, Yaacob H. Cytotoxic Components of *Pereskia bleo* (Kunth) DC. (Cactaceae) Leaves. *Molecules.* 2009; 14(5):1713-24. doi: 10.3390/molecules14051713.
- Occupational vitiglio resulting from skin contact with rubber products containing this compound as an additive. O'Malley MA, Mathias CG, Priddy M, Molina D, Grote AA, Halperin WE. Occupational vitiligo due to unsuspected presence of phenolic antioxidant byproducts in commercial bulk rubber. *J Occup Med.* 1988; 30(6):512-6.

Benzophenone

- Known to the State of California to cause cancer (OEHHA Proposition 65 list, effective June 22, 2012, Labor Code mechanism). No NSRL listed.
- Previously observed to migrate into water from polypropylene bottles at room temperature, reaching concentrations up to 20 µg/L. Authors concluded no risk to human health. Skjevraak et.al, 2005).
- Evaluated for genotoxicity due to its detection in food products. Not found to be genotoxic. (Abramsson-Zetterberg & Svensson, 2011).

- Found to have low estrogenic and anti-androgenic activity (Suzuki et.al, 2005).

Phenanthrene

- IARC Classification: Group 3; *Not classifiable as to its carcinogenicity to humans*. IARC Monographs on the Evaluation of Carcinogenic Risks To Humans, Volume 92 (2010).
- U.S. EPA IRIS Classification: D; *Not classifiable as to human carcinogenicity*. Based on no human data and inadequate data from a single gavage study in rats and skin painting and injection studies in mice.
- Classified as persistent, bioaccumulative and toxic according to U.S. EPA (National Waste Minimization Priority PBT List) and Oregon Department of Environmental Quality.

2,2-Dimethoxy-1,2-diphenylethanone

- Significant estrogenic activity measured with an in vitro reporter gene assay (Wada et.al, 2004).

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