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Investigation of the primary plasticisers present in polyvinyl chloride (PVC) products currently authorised as food contact materials

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ABSTRACT

PVC is a common food contact material that is usually plasticised to increase its flexibility. Phthalates are one class of chemical compounds that are often used as plasticisers in PVC in a wide range of industries. They may be used in packaging materials for foods and can also be found in components of certain food processing equipment such as conveyor belts and tubing. Transfer of plasticisers from packaging to foods can occur. In recent years, there has been increased interest in understanding the health effects of phthalates, as well as the possible human exposure levels. However, there is limited information available about the routes of exposure to phthalates. In July 2014, the Chronic Hazard Advisory Panel (CHAP) produced a report for the U.S. Consumer Product Safety Commission detailing the potential health hazards of phthalates and phthalate alternatives. This report listed diet as one factor contributing greater than or equal to 10% of total phthalate exposure. As a result of this report, the U.S. Food and Drug Administration (FDA) is interested in determining the types of the primary plasticiser present in food packaging and processing materials as well as their concentrations. An investigation was conducted of 56 different samples of PVC food packaging and food processing materials available in the US market using a solvent extraction and GC-MS analysis. Nine different plasticisers including three phthalates, di(2-ethylhexyl) phthalate, diisononyl phthalate and diisodecyl phthalate, were identified in the products tested. The plasticiser concentrations ranged from 1 to 53% depending on the types of food contact materials and the type of plasticiser. Overall, it appears that manufacturers are switching away from phthalates as their primary plasticiser to alternate compounds such as ESBO, ATBC, DEHT, DINCH, DEHA and DINA.

Introduction

Polyvinylchloride, or PVC, is used to make a wide variety of consumer products including food packaging, cosmetics, toys and medical devices. As far as food contact materials, plasticised PVC can be found in food wraps, for both commercial and consumer use, conveyor belts and tubing, as well as in the gaskets found in metal cap closures used on glass jars and bottles. In its pure form, PVC is a rigid material much different than what consumers would associate with the flexibility of those products listed above. To get the flexible, stretchy consistency seen in plastic wraps and bags, plasticisers are added. Both phthalate and non-phthalate plasticisers can be added to the materials and are approved for use in the US under 21 CFR Parts **ARTICLE HISTORY**

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170-199 (Code of Federal Regulations 2017). These citations include regulations for plasticisers in polymeric substances as well as authorisations in food contact applications such as components of adhesives, resins and surface lubricants. It should be noted that the analysis and discussion here will concentrate on 1,2-benzenedicarboxylic acids (ortho-phthalates) which will be referred to as phthalates for the rest of this article. The other 1,3- and 1,4-benzenedicarboxylic acids (isophthalate and terephthalate) will be classified as nonphthalates. Approved phthalates include butyl benzyl phthalate (BBP), diisononyl phthalate (DINP), dicyclohexyl phthalate (DCHP), dihexyl phthalate (DHexP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP), diisodecyl phthalate (DIDP) and dibutyl phthalate (DBP).

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Some of the non-phthalate alternatives approved are diethylhexyl adipate (DEHA), diethylhexyl terephthalate (DEHT), acetyl tributyl citrate (ATBC) and epoxidised soybean oil (ESBO) (Code of Federal Regulations. Parts 2017). While all these plasticisers are approved for use in food contact materials, they are not approved for use as direct food additives.

In recent years, there has been an increase in concern due to several studies reporting effects of certain plasticisers on the endocrine and reproductive systems as well as the liver, especially in males (David et al. 2000; Voss et al. 2005; Niermann et al. 2015). It should be noted that these feeding studies were conducted at quite high doses and were only looking at the effects in rats and mice, not humans, upon exposure to phthalates, particularly DEHP (Center for Devices and Radiological Health 2001). Most of the concentrations used in the animal exposure studies are higher than published estimated human exposure concentrations. For example, David et al. (2000) saw the most drastic effects when the rats were fed food treated with 6000 ppm DEHP daily for 104 days. An additional study went even higher with their feeding concentrations and went from 3000 to 12,000 ppm DEHP (Ward et al. 1986). However, whether these observed health effects are a concern for humans has not yet been shown, and there are questions over how closely the reactions seen in mice and rats would mimic those in humans. There have been no studies to date which show any connection between human dietary exposure to phthalates and adverse health effects. Both the Centers for Disease Control and Prevention (CDC) and the National Institutes for Health believe that there is not enough data on the topic to decide whether low levels of phthalate exposure have any potential to cause problematic health effects in humans (Centers for Disease Control and Prevention. 2013; U.S. National Library of Medicine. 2017). The U.S. Food and Drug Administration (US FDA) published an assessment in 2001 that reviewed the risks from DEHP released from PVC medical devices (Center for Devices and Radiological Health 2001). In this safety assessment, it was concluded that there was little to no risk of health problems related to the migration of DEHP for most patients being treated with PVC medical devices. Those at highest exposure were those patients receiving longterm medical care involving plastic bags or tubing. The US FDA has not published a recent risk assessment regarding phthalates released from food contact materials.

One reason for increased awareness among consumers over the use of phthalates in the United States is the release of the 2014 Chronic Hazard Advisory Panel Report on Phthalates and Phthalate Substitutes (Chronic Hazard Advisory Panel on Phthalates and Phthalate Alternatives 2014). This report was mandated by the U.S. Congress and provided to the U.S. Consumer Product Safety Commission (CPSC). In the report, diet was included as one of several factors contributing to greater than 10% of total phthalate exposure. Other factors included personal care products, indoor air and dust. Due to this report, there was a permanent ban of some phthalates in concentrations greater than 0.1% in children's toys. Congress also recommended that any U.S. agencies responsible for the regulation of products containing phthalates and phthalate alternatives investigate the necessary risk assessments. To complete a proper risk assessment, data on the prevalence of these products in the marketplace are necessary. There are recent publications looking at the occurrence of phthalates and phthalate alternatives in food packaging in other countries around the world (Cao et al. 2014; Hanušova et al. 2015; and Fierens et al. 2012), but there has not been a recent analysis of products available on the U.S. market. These publications seem to show a trend worldwide of manufacturers moving away from the use of phthalates, particularly DEHP, and switching to the phthalate alternatives detailed above. To obtain occurrence data for products sold on the U.S. market, we analysed the primary plasticiser in 56 food contact materials. Both domestic and imported products were analysed to include a thorough market sampling of the products available to U.S. consumers. By presenting occurrence data for the primary plasticisers in food contact materials, this study will enable others to make accurate assessments regarding the current use

and work to better understand the dietary exposure of the U.S. population to these plasticisers.

Materials and methods

Reagents and materials

HPLC grade tetrahydrofuran (THF), hexane and cyclohexane were purchased from Fisher Scientific (Hampton, NH, USA). Analytical grade standards for the following compounds were purchased from Accustandard (New Haven, CT, USA): DBP, DEHP, BBP, DnOP, DINP and DIDP. Deuterated internal standards were also purchased from Accustandard: dibutyl phthalate-d4, di-(2-ethylhexyl) phthalate-d4 and di-n-octyl phthalate-d4. Benzyl butyl phthalated4 was acquired from CDN Isotopes (Quebec, Canada). BASF (Pasadena, CA, USA) provided the 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH). The remaining standards were purchased from Sigma Aldrich (St. Louis, MO, USA): di(2ethylhexyl) terephthalate (DEHT), diethylhexyl adipate (DEHA), ATBC, diisononyl adipate (DINA), cis,cis-11,12;14,15-diepoxyeicosanoate, methvl methyl tredecanoate, sodium methoxide, isooctane, cyclopentanone and boron trifluoride etherate.

Samples of films and gasket-containing products were acquired from grocery stores and international markets in the Greenbelt, MD area. An effort was made to get a collection of both domestic and international products that would contain plasticisers such as jarred foods and beverages. In instances of commonly consumed products such as beer and tomato sauce, brands were selected based on consumption trends reported by Nielson. Tubing/hoses and conveyor belts were ordered directly from suppliers from multiple areas of the United States in an effort to get a more representative sample.

Analysis of phthalates

CPSC's test method CPSC-CH-C1001-09.3 (Consumer Product Safety Commission 2010) was used with slight modifications to determine the presence of phthalates and other plasticisers in the gaskets. Briefly, a 50 ± 5 mg of sample was removed from the lid, tube or belt and placed into a sealable 20 mL glass vial having a screw cap closure with a PTFE septa. Five millilitres of THF was added to the vial and the vial was placed on a Glas-Col tube rotator for 30 min, rotating at $1 \times g$. In a few cases, samples were allowed to rotate for longer to ensure complete dissolution of the polymer. If no dissolution was evident, the sample was presumed to be a different plastic material than PVC. FTIR was used to identify the polymer and confirm that it was not PVC. Using a buret to allow dropwise addition, ten millitres of hexane was added to the vial. The vials were shaken and then allowed to sit for several minutes to allow the polymer to precipitate. To ensure that the sample was clean enough for injection into the gas chromatograph (GC), the THF/ hexane solution was filtered through a 0.45 µm PTFE filter into a clear glass 2.0 mL vial with a screw cap closure containing a PTFE septum. Varying volumes (0.3-1.3 mL) of filtered solution were combined with cyclohexane in a 2.0 mL vial (total volume, 1.5 mL) and screened with the GC-MS. Following determination of the plasticiser content of the sample, a new vial was prepared containing the internal standard for the corresponding sample plasticiser; at this time, adjustments were also made to the volume of extract added in order to ensure that the results would fall within the range of the calibration curve. Triplicate extractions were performed on each material.

Epoxidised soybean oil (ESBO) analysis

ESBO was extracted and analysed using a method with slight modifications to those of Castle et al. (1988) and Hanušova et al. (2013). Briefly, a 50 ± 5 mg portion of the sample was removed and placed into a 4 mL capped vial. The internal standard, 2 mg/mL methyl cis, cis-11, 12; 14, 15-diepoxyeicosanoate (0.125 mL), was added along with 1 mL of 20 mg/mL methyl tridecanoate. The vials were capped, inverted to mix and placed under a gentle stream of nitrogen and evaporated to dryness. Once dry, 3 mL of 0.02 M sodium methoxide was added to the vial for extraction and transmethylation. The vials were capped as before, inverted to mix and placed in a tube heater set to 60°C for 2 h. Once the reaction was complete, the vials were uncapped, the polymer removed and the solvent evaporated with nitrogen. In order to form the dioxolane derivatives, 1 mL of 2,2,4-trimethylpentane, 1.5 mL cyclopentanone and 0.5 mL boron trifluoride etherate were added. The vial was capped and then shaken for 30 s. In order to quench the reaction, 1 mL of 2 M aqueous NaCl was added and the vial was shaken for an additional 15 s. The layers were allowed to separate and then the top layer was transferred to a 2.0 mL vial for injection on the instrument.

GC-MS analysis of phthalates

The GC portion of the CPSC method was adjusted to include deuterated internal standards and other plasticisers beyond the six phthalates included in the initial publication. An Agilent 5975C gas chromatograph coupled to a 7890B mass spectrometer with a HP-5MS column (30 m \times 0.25 mm i.d. \times 0.25 μm film thickness) was used for the analysis. The oven was maintained at 50°C for 1 min, then ramped at 30°C/min to 280°C, followed by a 15°C/min ramp to 310°C and held for 5 min for a total run time of 15.7 min. Post run, the oven temperature was decreased to 110°C immediately. A constant flow of 1 mL/min of helium was employed. The inlet and mass-selective detector (MSD) transfer line temperatures were 290 and 280°C, respectively. The injection port split ratio was 10:1 and the injection volume was 1 µL. The injection liner was an ultra-inert, split, straight, glass wool liner (Agilent Technologies). Selected-ion monitoring (SIM) data were collected during the GC-MS analysis. Twelve ions in total were collected and divided into four different monitoring groups based on retention time. The group and ion information are included in Table 1. Calibration curves were prepared using the ratio of the peak areas of the plasticiser/IS versus concentration of the plasticiser. The calibration curves ranged from 2.5–80 μ g/g for all the plasticisers investigated except for DINA, DINP and DIDP. DINP and DIDP calibration curves ranged from 5 to 80 μ g/g and DINA curves ranged from 20 to 80 μ g/g.

For ESBO analysis, the GC portion of the Castle et al. (1988) and Hanušova et al. (2013) methods was adjusted for optimal performance with the instrumentation. The same instrument and column were used for the analysis as was previously described for the phthalate/alternate plasticiser analysis. The oven was maintained at 50°C for 1 min, ramped at 20°C/min to 300°C and held for 10 min for a total run time of 23.5 min. Post run, the oven temperature was decreased to 110°C immediately. A constant flow of 1 mL/min of helium was employed. The inlet and MSD transfer line temperatures were 290 and 280°C, respectively. The split ratio was 40:1 and the injection volume was 1 µL. SIM data were collected during the GC/ MS analysis. Four ions were monitored: the quantitation ions used were 277 and 309 for the ESBO derivative and methyl cis,cis-11,12;14,15-diepoxyeicosanoate derivatives, respectively; the confirmatory ions used were 309 and 337 for the ESBO derivative and methyl cis, cis-11,12; 14,15-diepoxyeicosanoate derivatives, respectively. Calibration curves were prepared using the ratio of the peak areas of ESBO/IS versus mg ESBO extracted. The calibration curves ranged from 4 to 20 mg of ESBO.

For phthalate and non-phthalate containing samples, concentrations in the gasket were determined by normalising the phthalate response using the response of the internal standard and using the following formula:

| | · · · · · · | | • |
|----------|--|----------------------|---------------------------|
| Compound | Internal standard | Retention time (min) | lons |
| DBP | DBP-d4 | 8.4 | 149 ^a -223-205 |
| DHexP | DhexP-d4 | 9.7 | 149 –251 |
| BBP | BBP-d4 | 9.8 | 149 –206 |
| DEHP | DEHP-d4 | 10.4 | 149 –167–279 |
| DCHP | DCHP-d4 | 10.4 | 149 –167 |
| DnOP | DnOP-d4 | 11.0 | 149 –279 |
| DINP | DnOP-d4 | 11.4 | 293 –127 |
| DIDP | DnOP-d4 | 11.8 | 307 –141 |
| DEHA | DEHP-d4 | 9.8 | 129 –112 |
| DEHT | DEHP-d4 | 11.0 | 149 –167–261 |
| DINCH | Benzyl benzoate (BB) | 11.5 | 155 –127 |
| ATBC | Benzyl benzoate (BB) | 9.4 | 185 –129–259 |
| DINA | Benzyl benzoate (BB) | 10.4 | 129 –147–207 |
| ESBO | Methyl cis, cis-11,12;14,15-diepoxyeicosanoate | 16.6 | 277 -309 |

Table 1. Internal standard as well as confirmation and quantitative ions for 14 different plasticisers.

^aThe quantitative ion is listed in bold followed by the additional confirmation ions.

% Phthalate
$$\left(\frac{w}{w}\right) = \left[\frac{C * V * D}{W * 1000}\right] * 100$$

where *C* is the concentration output from the calibration curve, *V* is the total volume of THF/hexane (15 mL), *D* is the dilution factor based on the volume added to the 2.0 mL vial, and *W* is the mass of the PVC sample collected (in mg).

For ESBO-containing samples, concentrations in the gasket were determined by normalising the ESBO response using the response of the internal standard and using the following formula:

$$\% ESBO\left(\frac{w}{w}\right) = \left[\frac{M_c}{M_p}\right] * 100$$

where M_c is the mass of ESBO extracted in mg derived from the calibration curve and M_p is the mass of the PVC sample analysed (in mg).

FTIR

For those samples that did not dissolve in THF, it was presumed that the polymer was not PVC. These polymers were further analysed using FTIR in order to make a valid identification of the material. Infrared spectra were collected with a Nicolet 6700 FTIR spectrophotometer (Madison, WI, USA) with an attenuated total reflectance (ATR) (Thermo Scientific, Madison, WI, USA) attachment and a diamond ATR crystal. Prior to each analysis day, a background spectrum was collected to be used for background subtraction from the collected sample spectra. In order to ensure that there was no carryover between samples, the surface of the diamond crystal was cleaned prior to each analysis with ethanol. The spectrometer was operated with OMNIC 8.3 software (ThermoFisher Scientific) to collect spectra in the range from 4000 to 400 cm^{-1} . Polymers were identified by comparing the sample spectra with polymer IR libraries and standard reference materials.

Results and discussion

Prior to beginning sample analysis, a prototype of a new standard reference material (SRM, plasticised PVC), provided by NIST, was used to ensure that the method performance was acceptable. Three SRMs were used for the analysis: a blank PVC, a 0.1% phthalate PVC and a 2.0% phthalate PVC material. Each of the phthalate-plasticised SRMs contained six different phthalates at the known concentrations: DBP, BBP, DEHP, DnOP, DINP and DIDP. All materials were plasticised to the same total concentration using DEHA. The blank response for all phthalates was determined to be less than the lower limit of quantitation (LLOQ) for the method (0.03%) based upon the limits of the calibration curve. The limits of detection for this method were not investigated since no analyses were being conducted at trace concentrations.

Figure 1 illustrates the average recovery and standard deviation for the 0.1 and 2.0% materials. The recoveries ranged from 82 to 110% and 92 to 102% for the 0.1 and 2.0% materials, respectively. The deviations on the figure indicate interday repeatability as the three replicates were completed across different days. Three replicates were also completed on the third day in order to collect intraday repeatability data. The % RSD_r ranged from 0.47 to 3.88% and 0.26 to 1.40% for the 0.1% and 2.0% samples, respectively. The % RSD_R ranged from 8.49 to 17.25% and 1.13 to 9.21% for the 0.1% and 2.0% samples, respectively. The standard deviations were larger for DINP and DIDP than the other phthalates. This was not surprising because those compounds are isomeric mixes and must be manually integrated causing a greater variation in the concentrations.



Figure 1. Percent recovery of six different phthalates from three NIST Standard Reference Materials (SRMs) containing blank, 0.1% or 2.0% phthalates. Average recovery values are shown (n = 3) and the error bars represent the standard deviation.

Fifty-six products were analysed in order to identify and quantify their primary plasticiser. No additional plasticisers were observed in the samples above a concentration of 0.1%. These products were divided into five categories: tubing and belts, non-alcoholic bottled beverages, bottled beer, food wraps and jarred food products. Both domestic and international products were purchased and included products from 14 countries. Three phthalates were found in the products: DEHP, DINP and DIDP at concentrations ranging from 6 to 53%. Overall, it appears that manufacturers are switching away from phthalates as their primary plasticiser to alternate compounds such as ESBO, ATBC, DEHT, DINCH, DEHA and DINA.

Two types of food wraps were investigated: food service wraps and commercial wraps. Food service wraps are those that would be found wrapping meat, vegetables or sandwiches at grocery stores and delis. Commercial wraps are those that can be purchased by consumers at major grocery stores across the country. Of the four food service wraps investigated, only three were PVC (Table 2). The fourth was determined to be low-density polyethylene (LDPE) using FTIR. All three of the PVC wraps contained DEHA as their primary plasticiser, with concentrations ranging from 14.1 \pm 1.8% to 20.2 \pm 4.5%. Of the three commercial wraps evaluated, there was only one that was determined to be PVC. The other two were also LDPE. In contrast to the food service wraps, the primary plasticiser in the PVC wrap was DINA, but the concentration was similar to those of the DEHA in the food service wraps.

 Table 2. Primary plasticiser and concentration for food service and commercial wraps.

| Product | Country of origin | Primary plasticiser | Concentration (%) ^a |
|-------------------------|-------------------|------------------------|-----------------------------------|
| Food Service Wrap #1 | USA | DEHA | 14.1 ± 1.8 |
| Food Service Wrap #2 | USA | DEHA | 20.2 ± 4.5 |
| Food Service Wrap #3 | USA | DEHA | 17.6 ± 5.8 |
| Commercial Wrap #1 | USA | DINA | 13.1 ± 3.5 |
| Commercial Wrap #2 | USA | Not PVC | N/A^b |
| Commercial Wrap #3 | USA | Not PVC | N/A |
| Food Service Wrap #4 | USA | Not PVC | N/A |

^aConcentrations were determined in triplicate. Mean \pm standard deviation. ^bN/A = not applicable because no plasticisers present since not PVC.

The data of the present study found similar results to that of a 2014 Canadian study by Cao et al. In that study, 118 samples of wraps used to contain beef, pork, chicken, fish and cheese were analysed. The authors reported that both plasticised PVC wraps and some non-plasticised wraps, which the authors assumed to be polyethylene films, were found. None of the wraps contained phthalates. The only plasticiser the authors reported finding in the wraps was DEHA. It should be noted however that they were only looking for DEHA as well as eight different phthalates. Therefore, it cannot be concluded whether DINA was present in the samples. Based on a study published by Page and Lacroix (1995), PVC wraps were one of the first categories of plasticised PVC to replace phthalate plasticisers with non-phthalate alternatives such as DEHA. The authors analysed the occurrence data for numerous types of plasticised PVC and found that 31 samples of wraps contained DEHA as the primary plasticiser. The samples in the Page and LaCroix study were collected from 1985 to 1989, signifying that the plasticised wraps seen in the present study are consistent with what has been observed in samples for the previous 30 years.

Five samples each of tubing and conveyor belts, which were advertised as approved for use as food contact materials, were purchased from suppliers spread across the United States. All five of the conveyor belt samples contained DINP as the primary plasticiser (Table 3). There were two grades of flexibility for the conveyor belts and this was reflected in the concentrations of the plasticisers. The two more

 Table 3. Primary plasticiser and concentration for tubing and conveyor belts sold for use as food contact materials.

| conveyor bens sold for use as food contact materials. | | | | |
|---|-------------------|---------------------|--------------------------------|--|
| Product | Country of origin | Primary plasticiser | Concentration (%) ^a | |
| Tubing #1 | USA | DEHP | 41.1 ± 1.9 | |
| Tubing #2 | USA | DEHP | 30.4 ± 1.5 | |
| Tubing #3 | USA | DEHP | 43.7 ± 1.4 | |
| Tubing #4 | USA | ATBC | 38.3 ± 9.6 | |
| Tubing #5 | USA | DIDP | 37.4 ± 6.6 | |
| Conveyor | USA | DINP | 6.0 ± 0.3 | |
| Belt #1 | | | | |
| Conveyor | USA | DINP | 5.7 ± 0.7 | |
| Belt #2 | | | | |
| Conveyor | USA | DINP | 31.6 ± 3.0 | |
| Belt #3 | | | | |
| Conveyor | USA | DINP | 31.5 ± 3.3 | |
| Belt #4 | | | | |
| Conveyor | USA | DINP | 29.3 ± 6.6 | |
| Belt #5 | | | | |

 $^{\mathrm{a}}\mathrm{Concentrations}$ were determined in triplicate. Mean \pm standard deviation.

rigid belts had concentrations around 6%, while the three more flexible belts had concentrations near 30% DINP. There was more variability in plasticiser type observed in the tubing samples. Three of the samples contained DEHP, and there was one sample each containing ATBC and DIDP. The concentrations of these plasticisers were relatively similar between 30 and 45% regardless of plasticiser.

Six different non-alcoholic bottled beverages were tested, three domestic and three international products. The gaskets of the caps for these products were found to contain a broad range of plasticisers, with only one being repeated in the group of six, ESBO (Table 4). The other products contained DEHA, DEHP, DIDP or DINP. The concentrations of the phthalate and adipate plasticisers were determined to be approximately 40% in all four products. The ESBO-plasticised samples contained lower concentrations. One product contained 15.0 ± 3.1% ESBO and the other was $20.4 \pm 0.6\%$. Nine bottled beer samples were also evaluated (Table 5). The beers were selected based on US consumption rates in order to get data representing what a typical consumer might be exposed to. Seven of the beer bottles had gaskets that contained PVC and two had non-PVC gaskets. Both products were international beers and their gaskets were determined to be LDPE by FTIR. Most of the PVC gaskets contained DEHP

 Table 4. Primary plasticiser and concentration for cap gaskets of non-alcoholic bottled beverages.

| Product | Country of origin | Primary plasticiser | Concentration (%) ^a |
|--------------|-------------------|---------------------|--------------------------------|
| Soda #1 | Jamaica | DEHA | 39.6 ± 2.8 |
| Soda #2 | Mexico | DEHP | 40.9 ± 5.6 |
| Теа | USA | DIDP | 39.3 ± 5.5 |
| Soda #3 | USA | DINP | 39.9 ± 3.3 |
| Soda #4 | Jamaica | ESBO | 20.4 ± 0.6 |
| Coffee Drink | USA | ESBO | 15.0 ± 3.1 |

^a Concentrations were determined in triplicate. Mean \pm standard deviation.

 Table 5. Primary plasticiser and concentration for cap gaskets of bottled beer.

| Product | Country of origin | Primary plasticiser | Concentration (%) ^a |
|---------|-------------------|---------------------|--------------------------------|
| Beer #1 | USA | DEHP | 44.1 ± 9.5 |
| Beer #2 | Mexico | DEHP | 42.9 ± 4.9 |
| Beer #3 | USA | DEHP | 45.3 ± 4.9 |
| Beer #4 | Canada | DEHP | 44.6 ± 1.8 |
| Beer #5 | USA | DEHP | 45.4 ± 2.3 |
| Beer #6 | USA | DEHP | 46.1 ± 4.6 |
| Beer #7 | USA | DEHT | 24.4 ± 0.8 |
| Beer #8 | China | Not PVC | N/A ^b |
| Beer #9 | Netherlands | Not PVC | N/A |

^aConcentrations were determined in triplicate. Mean \pm standard deviation. ^bN/A = not applicable because no plasticisers present since not PVC.

Table 6. Primary plasticiser and concentration for cap gaskets of jarred food products.

| Product | Country of origin | Primary plasticiser | Concentration |
|------------------------|-------------------|------------------------|------------------------------------|
| Mustard | Cormany | | 5 6 ± 12 5 |
| Corret Chutney | India | ATDC | 3.0 ± 12.3 |
| Carlic Pasto #1 | Poru | ATBC | 0.9 ± 0.3 6 2 + 1 0 |
| Chili Boon Souce | China | ATRC | 0.2 ± 1.9 10.4 ± 4.5 |
| Salad Dressing | Germany | ATRC | 47 ± 0.8 |
| Adobo Sauce | Mexico | DEHD | $\frac{4.7 \pm 0.0}{38.0 \pm 2.4}$ |
| Garlic Paste #2 | India | DEHP | 35.0 ± 2.4 35.5 ± 1.3 |
| Fried Gluten | Taiwan | DEHT | 181 + 20 |
| Salsa Picante | Trinidad and | DINCH | 266 ± 24 |
| Suisa ricante | Tobago | Dirteri | 20.0 ± 2.1 |
| Gelatin Product | Philippines | ESBO | 28.2 ± 2.8 |
| Jerk Seasoning | Jamaica | ESBO | 36.5 ± 15.2 |
| Jam | Philippines | ESBO | 27.8 ± 2.3 |
| Honey #2 | Vietnam | Could not | N/A ^b |
| | | determine | |
| Applesauce | USA | DIDP | 48.8 ± 7.3 |
| Raspberry Preserves | USA | DIDP | 53.1 ± 0.6 |
| Baby Food #1 | USA | ESBO | 19.3 ± 4.0 |
| Baby Food #2 | USA | ESBO | 18.1 ± 3.8 |
| Baby Food #3 | USA | ESBO | 20.4 ± 1.8 |
| Marinara | USA | ESBO | 30.6 ± 7.3 |
| Sauce #1 | | | |
| Marinara | USA | ESBO | 23.0 ± 1.5 |
| Marinara | USA | ESBO | 30.0 ± 8.3 |
| Sauce #3 | | | |
| Peanut Butter | USA | ESBO | 27.0 ± 5.1 |
| Honey #1 | USA | ESBO | 33.3 ± 1.9 |
| Olives | USA | ESBO | 22.4 ± 4.9 |

^aConcentrations were determined in triplicate. Mean \pm standard deviation. ^bN/A = not applicable because no plasticisers present since not PVC.

as their primary plasticiser, but there was one brand that instead contained DEHT. The DEHP and DEHT concentrations were determined to be about 45% and 25%, respectively.

The largest category investigated was jarred food products, such as sauces, honeys and jarred vegetables. There were 11 domestic and 14 international products analysed (Table 6). Both the international and domestic products each contained only two products whose lids were plasticised with phthalates, DEHP for the international products and DIDP for the domestic products, respectively. There was an interesting divide between the plasticisers used for the remaining domestic and international products. All of the remaining domestic products contained ESBO as their primary plasticiser. The international products had much more variety in the plasticisers used in their gaskets: ATBC, DEHT, DINCH and ESBO were all represented. The concentration of the plasticiser found in the gasket varied by product but also type of plasticiser. The ATBC concentrations were overall significantly lower than those of other plasticisers, with most containing about 5% ATBC. The highest concentrations were found in the gaskets plasticised with DIDP, which contained $48.8 \pm 7.3\%$ and $53.1 \pm 0.6\%$. Most of the other plasticiser concentrations were in the 20–30% range.

No recent published occurrence data like that presented here was found for products available for purchase in the United States. However, there is some data available from surveys conducted in other countries. A large survey of products available for purchase in Canada published by Page and Lacroix (1995) covered numerous types of plasticised PVC products including jar lid gaskets collected from products purchased between 1985 and 1989. In contrast to what was seen in the current study, all but 19 of the 80 gaskets investigated contained DEHP as their primary plasticiser. The authors were only looking for six different phthalate plasticisers plus DEHA, so it is possible that these 19 gaskets were plasticised with an alternate plasticiser. It is interesting to note the dramatic decrease in DEHP from that observed in Canada in the late 1980s compared to what the present study observed in 2015 in the United States: the Canadian study observed 80% of the gaskets plasticised with DEHP, compared with only 8% in the present study. Analysis of gaskets taken from baby food jars showed a significant difference from the Canadian study. All three of the jars analysed in the present study contained ESBO as their primary plasticiser. The Canadian study also investigated baby food gaskets and found that the four samples purchased in 1987-1988 contained DEHP as their primary plasticiser but when five additional samples were purchased in 1988-1989 no DEHP was found in the gasket. Since the Canadian study was not analysing for ESBO, it is possible that baby food manufacturers were removing DEHP from the gaskets and replacing it with ESBO or some other non-phthalate plasticiser as early as 1988.

A more recent survey of gaskets of metal food closures was conducted in the Swiss market in 2006 by Fankhauser-Noti et al. (2006) These authors chose to concentrate their study only on oily foods contained in jars with metal food closures. Like the present study, the authors reported the main plasticiser present in the gasket. They found that ESBO was used most frequently at 64% of the gaskets, but other plasticisers were also found: epoxidised linseed oil (ELO, 7.4%), DEHP (15%), DINP (9%), DIDP (11%), DEHA (9%), acetylated partial glycerides (acPG, 2%) and DINCH (2%). Similar plasticiser variety and percentages were observed in other studies from the EU (McCombie et al. 2012), the Czech Republic (Hanušova et al. 2015) and Spain (Bueno-Ferrer et al. 2010).

Conclusions

The results of this study show that a wide variety of plasticisers are in use in products available for purchase in the United States. The US occurrence data presented here, along with the other more recent market surveys, show a switch since the 1989 Canadian data (Page and Lacroix 1995). It would appear that manufacturers are removing phthalates from jar gaskets and have been replacing them with non-phthalate alternatives. This trend can also be observed in NHANES data of urine concentrations of four metabolites of DEHP for survey years between 1999 and 2012 (National Center for Health Statistics. 2017. Fourth National Report on Human Exposure to Environmental Chemicals. [accessed 2017]). There is a sharp decline in the concentrations starting in the survey year 2005-2006 that continues for the rest of the years surveyed. The decrease in DEHP metabolites shows that the occurrence of DEHP in the environment, including food contact materials, has dropped off significantly since 2005. The market sampling presented here will provide valuable occurrence information needed for risk assessments regarding routes of exposure of the US population to phthalates and phthalate alternatives.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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