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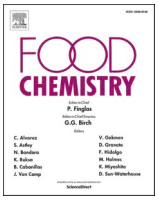

Targeted screening of 11 bisphenols and 7 plasticizers in food composites from Canada and South Africa

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ABSTRACT

A sensitive method based on ultrasound-assisted liquid extraction coupled with liquid chromatography was applied to screen 18 plastic-related contaminants in 168 food composites (namely fish fillets, chicken breast, canned tuna, leafy vegetables, bread and butter) collected in Montreal (Canada), Pretoria and Vhembe (South Africa). Bisphenol A (BPA), bisphenol S (BPS) and seven plasticizers (di-*n*-butyl phthalate (DBP), diethyl phthalate (DEP), (2-ethylhexyl) phthalate (DEHP), di-(2-ethylhexyl) adipate (DEHA), di-isononyl phthalate (DINP), di-(isononyl)-cyclohexane-1,2-dicarboxylate (DINCH)) were detected in different foods from both countries. DBP and DEP were the most frequently detected contaminants in food collected in Montreal (75% for both) and DINP was the most frequently detected contaminant in food from South Africa (67%). DEHA concentration in packaged fish were significantly higher than the values for non-packaged fish ($p < 0.01$) suggesting that the packaging film can be one source of DEHA in fish.

1. Introduction

Endocrine disrupting compounds (EDCs) are defined as exogenous chemicals that interfere with the endocrine system and disrupt the physiologic function of hormones (Sosa-Ferrera, Mahugo-Santana, & Santana-Rodríguez, 2013). Some bisphenols and phthalate esters which can mimic natural hormones and adversely affect endocrine function are recognized as typical EDCs (Gu et al., 2014). These classes of chemicals have been frequently detected in different types of foods and environmental samples (Liao & Kannan, 2013, 2014; Salgueiro-González et al., 2015; Schecter et al., 2013) and diet is reported to be a dominant source of human exposure to EDCs such as bisphenol A (BPA), di-(2-ethylhexyl) phthalate (DEHP) and diethyl phthalate (DEP) (Yang, Park, & Lee, 2006). Therefore, the occurrence of EDCs and their functional replacements in food should be monitored from a public health perspective.

BPA, the most well-known compound of the bisphenol family, is mainly used as a monomer in the manufacture of polycarbonate plastics and epoxy resins. Bisphenol analogues, chemicals with structures similar to that of BPA, are commonly used as substitutes for BPA. For example, bisphenol S (BPS), bisphenol F (BPF), bisphenol B (BPB) and bisphenol AF (BPAF) have all been used by the food packaging industry (Cunha, Cunha, Ferreira, & Fernandes, 2012; LaFleur & Schug, 2011). Most of the structural analogues of BPA have some effects on estrogen and androgen receptors at levels comparable to BPA (Rosenmai et al., 2014), which supports the need to monitor their levels in food. However, data for the occurrence and levels of BPA analogues in food are much less available than for BPA (Cao et al., 2019; Liao & Kannan, 2013, 2014; Viñas, Campillo, Martínez-Castillo, & Hernández-Córdoba, 2010). According to the literature, levels of BPA analogues in food are generally lower than 5 ng g^{-1} on a fresh weight basis (Liao & Kannan, 2013, 2014). However, in some exceptional cases, bisphenol analogues have been detected in food at relatively greater levels. For example, Liao and Kannan (2014) reported an average concentration of 15.4 ng g^{-1} for BPF

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in vegetables from nine cities in China, which was about 5 times higher than the concentrations of BPA detected in the same samples (2.9 ng g^{-1}).

Phthalates are a group of di-esters of ortho-phthalic acid. They are largely used as plasticizers in the manufacture of plastic materials for food packaging, medical devices, and personal care products (Staples, 2003). DEHP, a well-known phthalate, is widely used in plastic manufacturing (Yang et al., 2006). DEP and di-isononyl phthalate (DINP) are also important phthalate plasticizers in the plastic industry (Yang et al., 2006). According to the literature, DEHP is the most frequently detected contaminant in multiple foods among all the phthalates, followed by di-*n*-butyl phthalate (DBP) and DEP (Cheng et al., 2016; Fierens et al., 2012; Schecter et al., 2013). Due to concerns about the reproductive toxicity and endocrine disrupting properties of some phthalate plasticizers such as DEHP and DINP, the non-phthalate plasticizer, di-(isononyl)-cyclohexane-1,2-dicarboxylate (DINCH), has been applied in recent decades as the major alternative in the manufacturing of food contact materials, toys and childcare articles (Giovanoulis et al., 2018). According to a recent study by Giovanoulis et al. (2018), human exposure to DINCH is mainly from diet, but data on the occurrence of DINCH across different food categories are relatively scarce in the literature.

As bisphenols and plasticizers occur at trace levels in complex food matrices, highly selective and sensitive analytical methods are required for their detection and quantification. Effective sample preparation steps (extraction and clean-up) are crucial prior to the instrumental analysis. Methods based on high performance liquid chromatography (HPLC) or gas chromatography (GC) coupled to mass spectrometry (MS) are most frequently applied to the analysis of bisphenols and plasticizers in food matrices (Kozlowska-Tylingo, Namieśnik, & Górecki, 2010). In fact, LC-MS has become the state-of-the-art approach in recent years for analysis of trace contaminants in food (Cao et al., 2019; Kozlowska-Tylingo et al., 2010). A major challenge for the quantification of bisphenols and plasticizers in food is the ubiquitous occurrence of these compounds in the laboratory, including analytical solvents, plasticware or laboratory air (Schecter et al., 2013). Quality control samples and procedure blanks are therefore critical to assess and minimize background interference (Schecter et al., 2013).

In Canada, bisphenol and plasticizer levels have been reported mostly for packaged foods (Cao et al., 2011, Cao, Perez-Locas et al., 2015; Cao, Zhao, Churchill, & Hilts, 2014; Cao et al., 2019); information on their levels in non-packaged and raw foods from the Canadian market is limited. To the best of our knowledge, there is no literature published on the occurrence of bisphenols or plasticizers in food from South Africa.

The objective of the present study was to screen 11 bisphenols and 7 plasticizers in different food composites from markets in Montreal, Canada (2017–2019) and in Pretoria (urban) and Vhembe (rural), South Africa (2018). Samples from South Africa were included in the study to examine the difference in the levels of these contaminants in two countries. In the present study, contaminant levels were also compared between food items sold as packaged or not, where possible.

2. Materials and method

2.1. Reagents and standard preparation

Ammonium acetate (LC–MS grade), sodium sulfate anhydrous (purity ≥ 99%) and HPLC-grade solvents (water, acetonitrile and methanol) were purchased from Fisher Scientific (Hampton, NH, USA). Analytical standards of BPA (purity ≥ 99%), BPF (purity ≥ 98%), BPS (purity ≥ 98%), BPAF (purity ≥ 99%), bisphenol E (BPE, purity ≥ 98%), bisphenol P (BPP, purity ≥ 99%), bisphenol Z (BPZ, purity ≥ 99%), bisphenol AP (BPAP, purity ≥ 99%), bisphenol BP (BPBP, purity ≥ 98%), DEHP (purity ≥ 98%), DBP (purity ≥ 99%), DEP (purity ≥ 99%) and di-isodecyl adipate (DIDA, purity ≥ 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Bisphenol C (BPC, purity ≥ 98%), BPB (purity ≥ 98%), BPA-$^{13}C_{12}$ (purity ≥ 98%), BPF-$^{13}C_{12}$ (purity ≥ 98%), BPS-$^{13}C_{12}$ (purity ≥ 98%), BPAF-d_4 (purity ≥ 98%), DINP (purity ≥ 98%), DINCH (purity ≥ 98%), di-(2-ethylhexyl) adipate (DEHA, purity ≥ 98%), DEHP-d_4 (purity ≥ 97%), DBP-d_4 (purity ≥ 99%), DEP-d_4 (purity ≥ 99%), DINP-d_4 (purity ≥ 99%) and DEHA-d_8 (purity ≥ 99%) were purchased from Toronto Research Chemicals (Toronto, ON, Canada). DINCH-$^{13}C_4$ (purity ≥ 99%) was purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). Stock solutions of all individual standards were prepared in methanol (100 mg L^{-1}). Working standard mixture solutions of the 11 native bisphenols and 7 plasticizers were prepared weekly at a concentration of 1 mg L^{-1} in methanol. The labeled standard mixture solution containing 10 mass-labeled surrogates was prepared weekly at a concentration of 1 mg L^{-1} in methanol. Standard solutions were stored in amber glass vials in the freezer (−20 °C).

2.2. Background contaminant control

To avoid background contamination during the food sample processing, laboratory tools were cleaned and/or baked before use; the detailed procedures have been described in our previous study (Tian, Zheng, Goodyer, & Bayen, 2020). Sodium sulfate anhydrous was prepared following the same procedure as for the food composite preparations (see section 2.3); this was used for procedure blank extraction. Solvent blanks (n = 3) and procedure blanks (n = 5) were analyzed in triplicate across the sample batch to monitor background contamination. The highest blank values were subtracted from the concentrations measured in food composite samples (Schecter et al., 2013), an approach which may slightly underestimate the actual concentrations in real samples.

2.3. Food sampling, sample preparation and food composite extraction

2.3.1. Food sample collection

Six types of packaged food, namely fish fillets, chicken breast, canned tuna, leafy vegetables, bread and butter, and two types of “non-packaged” food (fish fillets and vegetables sold in an unpackaged form in the retail markets), were purchased from different local markets in Montreal, Canada over four sampling rounds from 2017 to 2019 (see Supplementary material, Table S1 for detailed information). Whenever possible, the same types of packaged and “non-packaged” food were collected. Similar types of food samples (except butter and chicken) were also purchased from markets in Pretoria and Vhembe in South Africa between September and November 2018 (see Supplementary material, Table S2).

Packaged foods were purchased directly from the markets and transported in a cooler with ice packs. “Non-packaged” fish fillets and vegetables were wrapped in aluminum foil at the point of sale before being transported to the laboratory. In addition, the cores of the bread loaves (not in direct contact with packaging) were isolated from the outer layers using a stainless-steel knife. The two resulting samples were then processed into composites as described below to investigate any potential differences between the core and the outer layers of bread. Similarly, the cores and the outer layers (1 cm) of butter (salted and unsalted) were separated to investigate the levels of contaminants in the two portions.

2.3.2. Food composite preparation

To screen the occurrence of food contaminants in human diet, food composites were commonly used when the sample size is large, and this is one of the most cost-effective approach to assess dietary intakes of some toxic chemicals. However, as foods are composited and the levels of contaminant in individual foods and the variability across brands cannot be achieved (Cao et al., 2011).

Samples collected in Montreal (n = 504) were stored in a fridge (4 °C) as soon as they arrived in the lab, and composites were created

within 24 hrs. A stainless-steel manual meat grinder was used to grind fish fillets and chicken breast samples. Vegetables, bread and butter samples were cut on aluminum foil using a stainless-steel knife. Canned tuna samples were stirred and mashed by a stainless-steel spatula. For each sampling round, a composite was produced using about 30 g (±1 g) of each prepared individual food samples and transferred into a 250-mL amber glass jar. The composite was then freeze-dried (Martin Christ Gamma 1–16 LSC freeze-dryer, Osterode am Harz, Gemany), and further homogenized using a mortar and pestle. The food composites were transferred into an amber glass jar and aluminum foil was inserted between the samples and the polypropylene lids prior to storage at −80 °C. Aliquots of each prepared individual food sample were wrapped in aluminum foil and vacuum-sealed in a polypropylene bag before storage in a freezer (−80 °C).

Packaged and non-packaged food samples from South Africa (n = 117) were entirely wrapped in aluminum foil and kept in a freezer (−80 °C) before being shipped to Canada on dry ice. Food samples were thawed on ice and food composites were prepared following the same procedure as described above.

2.3.3. Extraction

Composite samples were extracted using the ultrasound-assisted liquid extraction method, following the procedure reported in our previous study with some modifications (Tian, Verreault, Houde, & Bayen, 2019). In brief, 0.5 g (±0.05 g) of each freeze-dried food composite was weighed into a 15-mL polypropylene centrifuge tube. Mass-labelled surrogate standards were spiked into the composites (representing about 60 ng g^{-1} of fresh food) prior to extraction. Then, 6 mL of methanol were added and the tube was vortexed for 1 min using a Vortex Mixer (Fisher Scientific, Hampton, NH, USA). After vortexing, the tubes were placed in a Branson 3510 sonication bath (40 kHz) for 30 min and samples were centrifuged at 4500 rpm for 10 min (IEC, Needham Heights, MA, USA). Finally, the supernatant was collected, filtered through a 0.22 μm filter (Norm-Ject, Tuttlingen, Germany) directly into HPLC amber glass vials and stored at −20 °C until HPLC analysis.

Vegetable composites were extracted following the same procedure as above except that acetonitrile was used instead of methanol, which resulted in higher analyte recoveries. After filtration into the HPLC amber glass vials, the extracts were dried under nitrogen gas, reconstituted in water/methanol (v/v = 1:1) and kept at −20 °C until HPLC analysis.

2.4. Instrumental analysis

Electrospray ionization in negative mode is required for the LC-MS analysis of bisphenols, while phthalates, DEHA and DINCH are to be analyzed in positive mode. The instrument analyses of these two groups of compounds were performed according to methods adapted from earlier work in our laboratories.

2.4.1. Instrumental analysis for bisphenols

Samples were analyzed using an Agilent 1290 Infinity II LC system (Agilent Technologies, Santa Clara, USA) coupled to a 6545 quadrupole time-of-flight (Q-TOF) MS (Agilent Technologies, Santa Clara, USA) to screen for bisphenols in food. The detailed method has been published earlier (Tian et al., 2020) (Table S3). LC-QTOF-MS data were analyzed using Agilent MassHunter Quantitative analysis (B.07.01) software to quantify eleven bisphenol analogues in food samples and procedural blanks. The most abundant isotopes of $[M-H]^-$ were used as quantifier for the eleven bisphenols. The chromatogram extraction window was ± 10 ppm for mass and ± 0.5 min for retention time (RT).

2.4.2. Instrumental analysis for plasticizers

The concentrations of phthalates in the extracts were measured by LC-HRMS. The chromatographic separation of the target compounds was done using the method described in Bissegger, Castro, Yargeau, and Langlois (2018). Briefly, the chromatography separation was performed on an Accela 600 LC system (Thermo Scientific, Waltham, MA, USA) with a Zorbax HDHR Eclipse plus C18 column equipped with a C18 Eclipse plus (12.5 × 2.1 mm ID., 1.8 μm) guard column and an isolator column (Agilent Technologies, Santa Clara, CA, USA). MS detection was performed on an LTQ Orbitrap XL (Thermo Fisher Scientific, Waltham, MA) with a heated electrospray ion source (HESI) operated in positive mode. The acquisition of data was done in full scan mode (50–800 m/z) in high resolution (FTMS resolution @ 30,000) and a simultaneous MS/MS scan was performed on the linear ion trap for structural product ion confirmation. Quantification of the analyte was carried out by extracting the ion of interest using an m/z range of ± 5 ppm accuracy and confirmation by MS/MS spectra. For each compound, a six-point calibration curve was generated in the range of 1–150 μg L^{-1}. The Thermo Xcalibur software (Thermo Scientific, Waltham, MA, USA) was used to analyze the data.

2.5. Quality assurance and method validation

Quality assurance for the analyses included the control of background contamination (section 2.2), and the monitoring of mass accuracy, intensity and RT shifts and signal drift using the repeated analysis of calibration standards and spiked samples (QCs) every 20 injections. One sample of each type of food (namely high-fat fish, low-fat fish, vegetable, chicken breast, brown bread, white bread, canned tuna in oil, canned tuna in water and butter) was randomly selected as a QC ($n = 9$). Both the native standard mixture solution and the labeled standard mixture solution were spiked into the QCs (also representing about 60 ng g^{-1} fresh weight for each compound) before the extraction.

To validate the performances of the instruments for the 18 target compounds, six calibration standards (5 to 150 μg L^{-1} of the target analytes, 60 μg L^{-1} for the mass labeled surrogates) were assessed in both pure solvents and food extracts. The linearity of the instrument response was assessed using the response of the calibration standards prepared in methanol. The method detection limit (MDL) was calculated as three times the standard deviation of procedural blanks. If the analyte was absent in all procedure blanks, the MDL was determined as the concentration of the target analyte in food extracts that yielded an ion signal-to-noise of three. Matrix effects for all food matrices were evaluated by comparing the matrix-matched calibration curves with the calibration curve prepared in pure solvents. Matrix effect smaller than 20% is treated as mild effect (Kmellár et al., 2008). The recoveries for all target compounds in different food matrices were calculated using the internal standard method which can correct for the matrix effect (Diana Di Mavungu et al., 2009). The relative standard deviation (RSD) for the inter-day precision was calculated based on the analysis of three replicates of QCs ($n = 9$) on different days. An inter-day precision (RSD) lower than 15% was judged acceptable (Rezk, Safa'a, Khattab, & Marzouk, 2015).

2.6. Statistical analysis

A comparison of contaminant patterns in foods sampled from the three different locations was not conducted due to the limited number of samples from South Africa. Statistical analysis was only carried out for foods sampled in Montreal. Two-way ANOVA ($p < 0.05$) was performed using IBM® SPSS Statistics (version 22.0) to investigate the relationship between contaminant concentration and packaging form in different food composites. Principal component analyses (PCAs) were conducted using SigmaPlot v.14 (Systat, San Jose, CA, USA) to understand the variability of contaminants amongst the various food matrices. Values of MDL/$\sqrt{(2)}$ or MDL/2 are reported in the literature for imputation for non-detects (Hornung & Reed, 1990; Liao & Kannan, 2013). In the present study, both types of imputations were tested in the PCAs investigating contamination patterns among food types, and the type of imputation did not impact the interpretation (see section 3.4, Figure S2

Table 1
Mean concentration of contaminants (ng g^{-1}, fresh weight) in different food composites from markets in Montreal (Canada).

Food category	Sample name	Type	N[#]	BPA	BPS	DBP	DEP	DEHA	DEHP	DINP	DINCH	DIDA
Fish	Basa	P	4	ND	14.0 ± 17.3	3.62 ± 4.77	31.8 ± 27.8	136 ± 106	3.16 ± 2.02	28.3 ± 20.1	2.05 ± 2.19	ND
	Basa	NP	2	ND	11.6 ± 7.7	21.2 ± 29.9	25.2 ± 35.6	148 ± 151	8.70 ± 5.65	1.95 ± 1.39	2.36 ± 3.12	ND
	Cod	P	4	4.34 ± 8.08	23.3 ± 26.9	4.89 ± 7.55	7.99 ± 15.8	190 ± 62.1	1.72 ± 2.49	0.87 ± 0.86	1.04 ± 1.05	ND
	Cod	NP	4	ND	19.4 ± 33.8	1.85 ± 2.38	28.5 ± 29.2	26.3 ± 37.8	1.02 ± 1.55	0.13 ± 0.16	0.64 ± 0.97	ND
	Haddock	P	4	ND	11.5 ± 22.7	1.81 ± 2.40	21.7 ± 23.0	201 ± 80.9	0.98 ± 1.63	7.39 ± 3.98	ND	ND
	Haddock	NP	4	ND	ND	1.68 ± 2.39	21.4 ± 18.5	9.6 ± 10.2	2.71 ± 1.31	8.66 ± 8.23	ND	ND
	Hake	P	2	ND	46.9 ± 66.3	25.8 ± 36.3	20.1 ± 28.3	325 ± 11.4	0.46 ± 0.58	3.23 ± 4.49	ND	ND
	Halibut	P	2	ND	ND	ND	21.3 ± 30.0	150 ± 49.9	0.70 ± 0.28	28.5 ± 31.2	ND	ND
	Halibut	NP	3	ND	ND	3.85 ± 5.44	24.1 ± 35.4	17.1 ± 24.4	ND	0.22 ± 0.30	5.70 ± 9.61	ND
	Rainbow trout	P	4	ND	9.58 ± 13.4	6.06 ± 7.41	24.0 ± 25.8	259 ± 84.7	1.46 ± 1.37	5.41 ± 4.81	2.23 ± 2.59	ND
	Rainbow trout	NP	4	ND	ND	4.48 ± 6.35	69.1 ± 21.1	105 ± 201	ND	0.83 ± 0.96	0.75 ± 1.21	ND
	Salmon	P	4	ND	22.2 ± 31.2	9.46 ± 8.80	18.2 ± 36.3	581 ± 261	ND	14.2 ± 20.2	4.23 ± 5.33	ND
	Salmon	NP	4	ND	7.51 ± 14.7	2.85 ± 3.24	6.55 ± 12.9	9.0 ± 2.5	ND	2.74 ± 4.56	3.06 ± 3.72	0.23 ± 0.37
	Sole	P	4	ND	27.1 ± 27.8	2.32 ± 1.42	34.0 ± 40.8	409 ± 139	3.93 ± 2.06	0.36 ± 0.30	ND	ND
	Sole	NP	4	ND	1.96 ± 3.63	2.96 ± 2.42	27.9 ± 35.6	64.8 ± 105	7.36 ± 7.78	20.5 ± 36.2	ND	ND
	Tilapia	P	4	ND	28.8 ± 33.7	6.17 ± 9.44	36.7 ± 27.8	235 ± 178	1.62 ± 1.43	23.4 ± 19.2	2.72 ± 5.14	ND
	Tilapia	NP	4	ND	8.34 ± 16.4	2.32 ± 1.37	26.6 ± 30.9	26.3 ± 21.7	3.71 ± 4.75	39.7 ± 44.1	0.89 ± 1.48	0.27 ± 0.45
Vegetable	Arugula	P	4	ND	ND	4.50 ± 4.61	8.66 ± 7.14	0.51 ± 0.92	0.83 ± 0.93	ND	0.85 ± 1.40	0.33 ± 0.51
	Arugula	NP	3	ND	ND	4.99 ± 2.48	14.0 ± 12.3	ND	0.24 ± 0.32	ND	3.58 ± 5.93	ND
	Romaine lettuce	P	4	ND	ND	2.33 ± 1.13	10.7 ± 11.6	ND	0.63 ± 0.82	ND	2.60 ± 4.99	ND
	Romaine lettuce	NP	4	ND	ND	3.01 ± 1.81	12.6 ± 14.4	2.55 ± 3.63	0.40 ± 0.52	0.66 ± 0.92	2.86 ± 3.22	ND
	Spinach	P	4	ND	ND	5.49 ± 4.35	9.74 ± 11.2	ND	0.14 ± 0.21	0.11 ± 0.14	ND	ND
	Spinach	NP	4	ND	ND	4.95 ± 3.38	0.89 ± 1.63	1.37 ± 1.56	0.36 ± 0.73	0.45 ± 0.50	ND	0.31 ± 0.51
	Watercress	P	3	ND	0.17 ± 0.12	3.29 ± 1.65	11.0 ± 14.4	0.36 ± 0.56	0.74 ± 0.72	0.39 ± 0.62	ND	0.41 ± 0.58
	Watercress	NP	3	ND	ND	3.02 ± 2.40	6.43 ± 11.0	1.26 ± 1.13	0.71 ± 0.73	1.10 ± 1.21	ND	0.32 ± 0.42
Bread	Whole wheat bread	P*	4	ND	ND	28.1 ± 27.8	97.6 ± 94.5	7.35 ± 6.33	ND	57.8 ± 60.8	8.32 ± 9.98	ND
	Whole wheat bread	P-C*	4	ND	ND	9.13 ± 16.5	53.6 ± 54.2	2.70 ± 5.39	1.62 ± 1.84	47.9 ± 67.1	5.21 ± 10.2	ND
	White bread	P*	4	ND	ND	9.09 ± 10.3	35.2 ± 51.1	ND	1.54 ± 2.11	45.8 ± 29.0	5.67 ± 6.67	1.38 ± 2.75
	White bread	P-C*	4	ND	ND	13.6 ± 22.1	11.9 ± 23.7	6.03 ± 7.16	ND	28.0 ± 21.2	4.67 ± 5.53	ND
Butter	Non-salted butter	P*	4	ND	ND	27.4 ± 43.0	146 ± 175	39.7 ± 47.7	7.33 ± 14.6	4.49 ± 8.90	793 ± 929	32.4 ± 49.5
	Non-salted butter	P-C*	4	ND	ND	6.71 ± 13.3	152 ± 120	10.9 ± 15.8	1.93 ± 3.79	1.53 ± 2.99	1160 ± 1390	22.7 ± 30.5
	Salted butter	P*	4	ND	ND	10.3 ± 18.8	65.0 ± 81.4	99.5 ± 121	17.1 ± 32.0	6.01 ± 7.09	920 ± 694	50.5 ± 40.9
	Salted butter	P-C*	4	ND	ND	3.08 ± 6.08	95.1 ± 139	22.1 ± 30.4	16.1 ± 32.1	ND	981 ± 877	4.12 ± 4.71
Chicken	Chicken breast	P	4	ND	18. 7 ± 34.3	2.73 ± 4.64	36.7 ± 24.5	254 ± 80.2	0.81 ± 1.55	16.2 ± 14.1	1.65 ± 1.85	ND
Canned tuna	Canned tuna in oil	P	4	ND	ND	3.76 ± 4.55	19.8 ± 39.5	ND	10.3 ± 11.8	29.8 ± 13.5	8.45 ± 9.74	ND
	Canned tuna in water	P	4	ND	ND	3.62 ± 2.72	6.82 ± 13.5	2.49 ± 3.49	4.57 ± 3.31	10.6 ± 2.61	ND	0.55 ± 0.93

Note: [#] N is the number of composites for each type of food. P: packaged; NP: non-packaged. * For bread and butter samples, P indicates the samples that have direct contact with packaging (outside layer), while P-C indicates the sample did not have direct contact with packaging (e.g. the core of packaged bread). ND: not detected.

ND represents cases where the contaminant levels were all below MDL for all food homogenates within the same category. ND is given instead of a MDL/2 value to give a clear definition of the absence of contaminants.

Table 2
Mean concentration of contaminants (ng g^{-1}, fresh weight) in different food composites from markets in South Africa.

Food category	Sample name	Type	N#	BPA	BPS	DBP	DEP	DEHA	DEHP	DINP	DINCH	DIDA
Fish	Anchovy	P	1	ND	ND	19.8	82.9	ND	3.86	22.4	ND	ND
	Bass	NP	1	ND	ND	ND	ND	ND	ND	0.47	ND	ND
	Bream	P	1	ND	ND	ND	ND	ND	ND	1.28	ND	ND
	Bream	NP	1	ND	ND	ND	25.6	17.5	ND	ND	ND	ND
	Catfish	NP	1	ND	ND	ND	7.4	ND	ND	ND	ND	ND
	Haddock	P	1	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Hake	P	2	ND	ND	ND	ND	ND	ND	0.75 ± 1.1	ND	ND
	Hake	NP	1	ND	ND	9.43	ND	81.3	ND	ND	ND	ND
	Mackerel	P	3	ND	ND	8.73 ± 10.3	7.5 ± 13.0	8.44 ± 14.6	ND	ND	1.48 ± 2.57	ND
	Salmon	NP	1	ND	ND	ND	ND	326	ND	ND	ND	ND
	Tilapia	P	2	ND	ND	ND	21.6 ± 30.5	0.32 ± 0.46	ND	0.2 ± 0.28	ND	ND
	Tilapia	NP	1	ND	ND	3.49	ND	ND	ND	1.26	ND	ND
Vegetable	Romaine lettuce	P	2	1.69 ± 1.97	ND	ND	17.8 ± 0.16	53.8 ± 76.1	0.46 ± 0.59	0.51 ± 0.66	2.73 ± 3.64	ND
	Spinach	P	1	11.3	ND	ND	ND	ND	ND	0.41	ND	ND
	Spinach	NP	2	4.74 ± 6.28	ND	ND	10.6 ± 15.0	1.49 ± 2.03	2.15 ± 0.19	5.51 ± 1.27	ND	ND
Bread	Whole wheat bread	P*	2	ND	ND	ND	80.2 ± 113	3.32 ± 4.62	ND	16.1 ± 2.0	123 ± 76.3	ND
	Whole wheat bread	P-C*	2	ND	ND	ND	79.7 ± 113	ND	ND	3.53 ± 2.12	74.1 ± 4.82	ND
	Whole wheat bread	NP*	1	ND	ND	ND	ND	ND	ND	2.5	24.1	ND
	Whole wheat bread	NP-C*	1	ND	ND	ND	ND	ND	ND	2.98	29.5	ND
	White bread	P*	1	ND	ND	ND	ND	243	ND	49.3	70. 9	ND
	White bread	P-C*	1	ND	ND	ND	ND	ND	ND	11.2	52.4	ND
Canned tuna	Canned tuna in oil	P	2	14.8 ± 20.6	ND	ND	63.5 ± 89.8	ND	ND	13.2 ± 0.60	ND	0.79 ± 1.01
	Canned tuna in water	P	2	11.7 ± 2.7	ND	1.16 ± 1.56	28.0 ± 39.4	ND	2.14 ± 1.59	10.6 ± 3.05	ND	ND

Note: # N is the number of composites for each type of food. P: packaged; NP: non-packaged. * For bread samples, P indicates the samples that have direct contact with packaging (outside layer), while P-C indicates the samples that did not have direct contact with packaging (e.g. the core of packaged bread); NP indicates the outside layer of non-packaged breads, while NP-C indicates the core of non-packaged breads. ND: not detected.
ND represents cases where the contaminant levels were all below MDL for all food homogenates within the same category. ND is given instead of a MDL/2 value to give a clear definition of the absence of contaminants.

and Figure S3).

3. Results and discussion

3.1. Method validation

Based on the calibration standards, the response of both instruments was linear ($r^2 > 0.98$) for all target compounds. Mean recoveries of the 18 compounds in food ranged from 70% to 129%. MDLs were lower than 0.6 ng g^{-1} (fresh weight) for all target compounds in all matrices which is comparable with previous reports in the literature (Cao et al., 2014; Schecter et al., 2013). The matrix effect for all the targeted compounds were mild in all food matrices (smaller than 5%), except for DIDA in butter (17.9% suppression) and in vegetables (10.2% suppression). The inter-day precision (RSD) was below 11.5%, which reflects a satisfactory precision for the analysis (Rezk et al., 2015). Details of the instrument linearity, recoveries and RSD for bisphenols have been reported elsewhere (Tian et al., 2020) and the detailed information for 7 plasticizers is presented in the Supplementary material (Table S4 and S5).

3.2. Targeted screening

3.2.1. Bisphenols in food composites

BPA and BPS were detected in food composites from both Canada and South Africa. The average concentrations of BPA and BPS in different food composites are shown in Table 1 and Table 2. Results were calculated as the average level of the contaminant in each type of food composite across four sampling rounds in Canada; MDL/2 was used if the contaminant level was lower than MDL (Hornung & Reed, 1990; Liao & Kannan, 2013). There was no contaminant concentration between MDL and limit of quantification in the present study. MDL/2 is recommended to be used for imputation for non-detects when the data are highly skewed (Hornung & Reed, 1990). None of the other bisphenols were detected in any food composites from the two countries.

BPA was detected in one single packaged cod composite from Canada (sampled in year 2017) but not in any other food composites from Canada. BPS was more frequently detected in fish and chicken composites in Canada across the four sampling rounds. The detection frequency of BPS (2017–2019) was 50% (16/32) and 24% (7/29) for packaged fish composites and non-packaged fish composites, respectively. The detection frequency of BPS in chicken composites in the four sampling rounds was 50% (2/4). Relatively high BPA concentrations were reported in a canned fish composite (109 ng g^{-1}, fresh weight) sampled in Canada in 2009 (Cao, Perez-Locas et al., 2015); but in the present study neither BPA nor the bisphenol analogues were detected in any of the canned tuna composites from Canada. This result is consistent with an action of removing BPA from food packaging in Canada (Cao et al., 2019). BPA has been reported in fresh fish from China (up to 11 ng g^{-1}, fresh weight) and Sweden (up to 29 ng g^{-1}, fresh weight) sampled in 2007 and 2005, respectively (Gyllenhammar et al., 2012; Niu, Zhang,

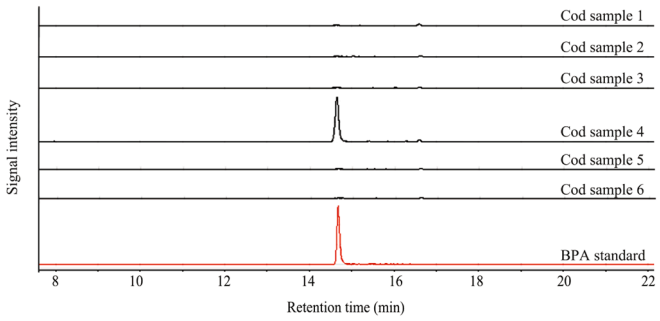

Fig. 1. BPA in individual cod samples from Montreal, Canada (sampled in May 2017).

Duan, Wu, & Shao, 2015). BPS was reported in fresh fish and meat products (including chicken) from both China and the US sampled in 2012 and 2008–2012, respectively; the mean concentrations of BPS in fresh fish and meat products from China (fish: 0.56 ng g^{-1}, meat: 2.16 ng g^{-1}, fresh weight) and the US (fish: 0.02 ng g^{-1}, meat: 0.61 ng g^{-1}, fresh weight) are lower than the mean values reported in the present study.

BPA was detected in several vegetable composites from South Africa: the detection frequency of BPA was two out of three in packaged vegetable composites and one out of two non-packaged vegetable composites. The levels of BPA in the vegetables from South Africa (up to 11.3 ng g^{-1}, fresh weight) were comparable with the values reported for vegetables sampled from China (up to 33 ng g^{-1}, fresh weight) and Spain (9.1 ng g^{-1}, fresh weight) (Mijangos, Bizkarguenaga, Prieto, Fernández, & Zuloaga, 2015; Niu et al., 2015). These results are not sufficiently representative to describe human exposure to BPA through vegetables in South Africa, due to the limited number of sampled vegetables; however, they do demonstrate the occurrence of BPA in vegetables in both a large city (Pretoria) and a rural area (Vhembe) of South Africa. BPA was also detected in canned tuna composites from South Africa (detection frequency 75%, 3/4), with concentrations up to 29.4 ng g^{-1} (fresh weight) (Table 2). BPA levels in canned tuna from South Africa were similar to those reported in Spain and the US (Alabi, Caballero-Casero, & Rubio, 2014; Noonan, Ackerman, & Begley, 2011). Unlike the samples collected in Canada, BPS was not detected in any food composites from South Africa (Table 2). It is reported that the BPA amount annually imported by South Africa is about 7 times as much as by Canada (World Integrated Trade Solution, 2018), which could be one of the reasons why BPA was present in more samples from South Africa than from Canada.

To confirm the presence of bisphenols in individual food samples as well as to validate the homogeneity of food composites, six individual cod samples and chicken breast samples (sampled in Montreal, 2017) used to prepare the composites were also extracted and analyzed. The result shows that BPA was present in only one cod sample at 92.1 ng g^{-1} (fresh weight), which is about 6-fold higher than the BPA concentration in the cod composite (Fig. 1). Similarly, BPS was detected in three out of six individual chicken breast samples, and the average level of BPS in the six individual chicken samples corresponded to the BPS level measured in the chicken composite. These results demonstrate that contaminant levels vary greatly between samples and that the contaminant concentrations reported in the present study accurately represent the average levels in food composites. A large variability of bisphenol levels in food has also been reported by Liao and Kannan (2013); the reason for this variability is not well understood as these contaminants can come into food through a variety of pathways and sources (Lu, Wu, Stoffella, & Wilson, 2015; Nerin, Alfaro, Aznar, & Domeño, 2013).

3.2.2. Plasticizers in food composites

None of the seven plasticizers was detected in solvent blanks. DEP, DEHP and DEHA were detected in the procedural blanks with the concentration ranging from 0.8 to 1.1 ng mL^{-1} for DEP (average = 1.0 ± 0.1 ng mL^{-1}), from 11.9 to 12.1 ng mL^{-1} for DEHP (average = 12.0 ± 0.05 ng mL^{-1}) and from 13.9 to 14.3 ng mL^{-1} for DEHA (average = 14.1 ± 0.05 ng mL^{-1}). The concentrations of these three compounds in food composites reported in the study have been corrected with highest blank values subtraction (Table 1 and Table 2). All seven plasticizers of interest were detected in food composites in both Canada and South Africa. Overall, these plasticizers were more frequently detected in food composites from Canada than from South Africa, as detailed below.

DBP and DEP were the most frequently detected plasticizers among all the food composites from Canada, with an overall detection frequency of 75% (100/134 food composites) for each of them across four sampling rounds. Relatively higher concentrations of DBP and DEP were detected in fish, butter and bread composites than the other matrices (Table 1). DBP levels in the present study were comparable with the data from the 2013 Canadian total diet study (TDS) (Cao, Zhao, & Dabeka, 2015). However, DEP concentrations in the present study (mean: 0.9–152 ng g^{-1}) were generally greater than those from the TDS in Canada (<18.2 ng g^{-1}) (Cao, Zhao et al., 2015) and Belgium (<9.3 ng g^{-1}) (Fierens et al., 2012). DEHA and DINP were also frequently detected in food composites in the present study with detection frequencies of 69% (92/134) and 63% (85/134), respectively. DEHA was detected in 97% (59/61) of the fish composites from Canada at levels up to 917 ng g^{-1} (fresh weight). DEHA levels in bread and vegetables were relatively lower (<16.3 ng g^{-1}), which is consistent with the literature (Cao, Zhao et al., 2015). DEHP was detected in 49% of the food composites, at relatively high levels in butter (up to 65.1 ng g^{-1}), but lower levels in other types of food (<20.6 ng g^{-1}). DEHP levels in the present study are relatively lower than those reported in the Canadian TDS in 2013 (Cao, Zhao et al., 2015) and lower than the values for multiple food types sampled in Belgium and China (Fierens et al., 2012; Sui et al., 2014). Data for DINCH and DIDA in food are limited in the literature. In the present study, DINCH and DIDA were mostly detected in butter composites from Montreal, with detection frequencies in butter of 87.5% (14/16) and 75% (12/16), respectively.

The detection frequencies for DINP and DINCH in food composites from South Africa were somewhat similar to the Canadian foods at 67% (22/33) and 30% (10/33), respectively; but their concentrations were generally lower than in the Canadian composites. DINCH was detected in all of the bread composites from South Africa, with concentrations ranging from 24.1 to 177 ng g^{-1}. DEP (detection ratio 12/33) and DEHA (detection ratio 9/33) were also detected in composites from South Africa, and their concentrations were lower than in the Canadian foods. The detection frequency for both DEHP and DBP was 18%. DBP was mainly detected in fish composites and its concentration in fish was similar to that in the Canadian fish (Table 1 and Table 2). DIDA was only detected in one composite (canned tuna) from South Africa with a concentration of 1.4 ng g^{-1}, which is comparable with the concentration of DIDA in canned tuna from Canada in the present study. As far as we know, this is the first time that DIDA has been detected in canned food.

Differences in the contamination patterns between the samples from the two countries are apparent but their origins remain to be identified. Limited background information is available in the literature on the occurrence of plasticizers in foods and food packaging in South Africa. BPA, DEHP and DEHA were reported in several cling films sold in South Africa (De Jager et al., 2019); however, how these films are used in their food industry is unknown. Food packaging could be one, but not necessarily the main or sole, reason for the differences in contamination patterns, which will be discussed in the section below (section 3.3). The analysis of food packaging materials from South Africa and Canada is an on-going project, and results will be reported in the future.

3.3. Comparison of DEHA levels in packaged and non-packaged food

A comparison of the contaminant levels in packaged and non-packaged food was undertaken using a two-way ANOVA test. Data for

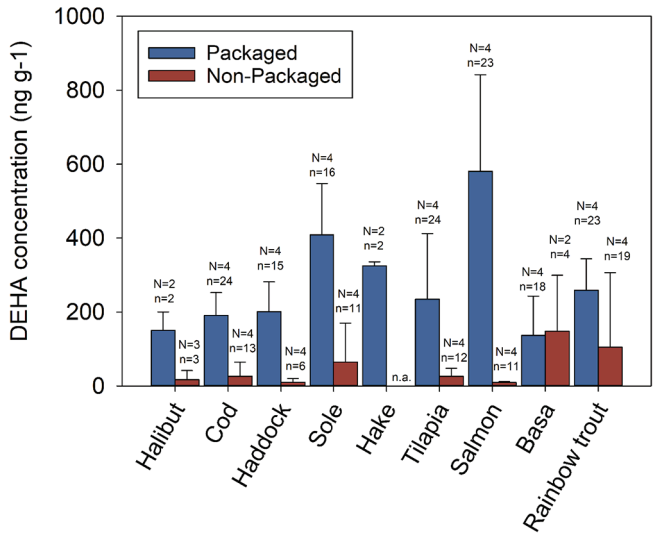

Fig. 2. Average DEHA concentration (ng g^{-1}, fresh weight) in fish composites from Canada. Note: "N" indicates the number of composites from four sampling rounds in Montreal; "n" indicates the number of individual fish samples in composites. The fish type is ranked by fat content from low fat (left) to high fat (right).

fish, vegetables, bread and butter composites from Canada were included. Composites that were missing one packaging type or did not have a normal distribution were not included.

The results indicate that DEHA concentrations in packaged fish were significantly higher than those for non-packaged fish ($p < 0.01$) (Fig. 2). This result is consistent with the literature as relatively higher DEHA concentrations were measured in fish wrapped under controlled conditions with plastic film as compared to fish not directly in contact with the plastic (Cao et al., 2014). The present result suggests that the packaging materials for market fish in Canada contain DEHA; analysis of these materials will be conducted in future studies.

None of the other target analytes showed any significant differences between packaged and non-packaged samples, or between the core and the outer layer for bread and butter samples. This suggests that the residues in these food products at the point of sale likely come from earlier contamination, in the environment, at the farm or during food processing.

3.4. Comparison of contaminant patterns in different food categories

A PCA based on the mean level for each type of food was conducted to understand the patterns among the different foods sampled in Montreal (both packaged and non-packaged). PCAs are commonly applied to determine contaminant patterns and to compare the variability (McKenzie, Rogan, Reid, & Wells, 1997). Principal components (PC) 1, 2, 3 and 4 explained 21.3, 15.0, 14.7 and 11.5% of the variability, respectively. Based on PC1 and PC2 (Fig. 3A), contaminant patterns in packaged fish and butter appeared to be different from the other foods. Similar interpretation could be derived from the plot for PC1 versus PC3 plot (not shown). These differences were mostly driven by BPS and DEHA in packaged fish and DEP, DINCH and DIDA in butter (see Supplementary material, Figure S1A). Packaged chicken breast also clustered with packaged fish (Fig. 3A), which suggests that the contaminant patterns in these various meat products are similar, possibly related to their common type of packaging at the point of sale.

Based on PC1 and PC4 (Fig. 3B), bread and butter samples also clustered as compared to the other commodities. The contributions of DBP and DINP in PC4 are mostly responsible for the clustering of the bread samples (see Supplementary material, Figure S1B).

4. Conclusions

In conclusion, the methods deployed in the present study enabled an effective screening of 18 plastic-related contaminants in 168 food composites (621 individual food samples). For the food samples from Canada, DBP and DEP were the most frequently detected contaminants, followed by DEHA and DINP. In contrast, DINP was the most frequently observed in South African foods. The results of the present study also indicate that packaging film is the possible source of DEHA in fish in Canada. BPA and BPS were the only bisphenols detected in any food composites. BPS concentrations in fresh fish and chicken samples from Canada were generally higher than the values reported earlier from the US and China. This is the first study to report bisphenol and plasticizer levels in foods from South Africa. Based on these findings, future research with a larger sampling size is highly recommended in order to obtain a comprehensive assessment of dietary exposure to these contaminants in South Africa. Finally, the results of the present study provide new information for food safety monitoring and exposure assessment in both Canada and South Africa.

CRediT authorship contribution statement

Lei Tian: Conceptualization, Formal analysis, Investigation, Methodology, Data curation, Writing – original draft, Writing – review &

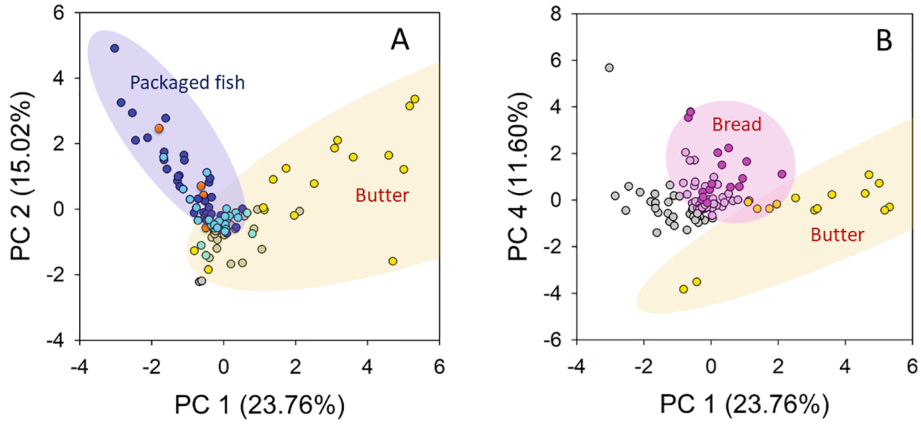

Fig. 3. PCA plot for all contaminants and all food matrices from Montreal, assuming a value of MDL/2 for non-detects. Figure A represents PC2 vs. PC1 with butter, chicken, packaged fish and non-packaged fish samples highlighted in yellow, orange, dark blue and light blue, respectively. Figure B represents PC4 vs. PC1 with butter and bread samples highlighted in yellow and pink, respectively. Samples other than the highlighted food categories are shown in grey dots.

editing. **Jingyun Zheng:** Formal analysis, Methodology, Data curation, Writing – review & editing. **Marco Pineda:** Formal analysis, Methodology, Data curation, Writing – review & editing. **Viviane Yargeau:** Conceptualization, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Resources, Writing – review & editing. **Daniel Furlong:** Formal analysis, Methodology, Data curation, Writing – review & editing. **Jonathan Chevrier:** Conceptualization, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Resources, Writing – review & editing. **Riana Bornman:** Conceptualization, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Resources, Writing – review & editing. **Muvhulawa Obida:** Conceptualization, Methodology, Project administration, Investigation, Data curation, Writing – review & editing. **Cindy Gates Goodyer:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Writing – review & editing. **Stéphane Bayen:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.132675.

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