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Assessment of heavy metals migrated from food contact plastic packaging: Bangladesh perspective

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ABSTRACT

Plastic-based food-contact materials are potentially threatening the environment and public health by releasing toxic heavy metals. This study aimed to identify the types of plastic commonly used in Bangladesh as food-contact materials (FCMs) and assess the migration of heavy metals from these FCMs. Plastic types were identified using attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), and 25 samples were selected based on the category, including Polyethylene Terephthalate (PET), Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), and Polycarbonate (PC). Distilled water, 3% acetic acid, and 15% ethanol were used as food simulants to assess the overall migration of chemicals at 70 °C for 2 h. The concentrations of heavy metals (Pb, Cd, Hg, Cr, and Sb) were analyzed using an Atomic Absorption Spectrophotometer (AAS). Results revealed that the highest overall migration occurred in coffee cups measuring 3.50 ± 0.17 mg/kg (using water simulant) and in yogurt containers with a measurement of 9.17 ± 0.1 mg/kg (using 3% acetic acid). The highest concentrations of Pb, Cd, Hg, Cr, and Sb were found in PP-2 (0.45 ± 0.01 mg/kg), PP-2 (0.36 ± 0.01 mg/kg), PC-5 (0.27 ± 0.01 mg/kg), PET-2 (0.12 ± 0.01 mg/kg), and PET-1 (0.09 ± 0.01 mg/kg), respectively. The concentration of heavy metals migrated from the containers is likely to induce a health risk due to bioaccumulation from long-term ingestion of food packaged in them. The findings of this study added knowledge about harmful heavy metals leached from the FCMs in Bangladesh.

1. Introduction

Plastics are widely utilized as food-contact packaging materials (FCPMs) on a global scale to maintain the freshness, aroma, and overall quality of food products during extended storage and transportation periods. The continuous increase in the use of plastic packaging materials (PPMs) has raised concerns about their impact on the environment and public health, particularly regarding food

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safety and non-biodegradability [1]. Commonly, various thermoplastics such as Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Polyethylene terephthalate (PET), Styrene acrylonitrile copolymer (SAN), Polyvinyl chloride (PVC), and Polycarbonate (PC) are used in the production of FCPMs. Additionally, thermosets such as melamine-formaldehyde (MF) resin and urea-formaldehyde (UF) resin are also utilized. The packaging materials can have different shapes and structures, such as films, sheets, and containers. They are made using various molding methods, such as blow molding, injection molding, extrusion, and casting. During the processing and manufacturing of durable plastic packaging materials, various additives, such as antioxidants, plasticizers, ultraviolet and thermal stabilizers, pigments, lubricants, and fillers, are typically mixed with virgin polymer. In the production of plastics, such as PVC, PE, PET, PP, and other unspecified types, catalysts such as Cr and Sb_2O_3 are commonly used in the polymerization process to enhance the quality of the materials [2]. Other metals such as cobalt (Co), manganese (Mn), nickel (Ni), lead (Pb), cadmium (Cd), antimony (Sb), and chromium (Cr) compounds are utilized in the recycling process of plastics and papers to enhance their physicochemical properties [3].

The FCPMs are, therefore, a diverse group of products that may contain a wide range of hazardous chemicals, such as heavy metals, phthalates, bisphenol A, formaldehyde, acetaldehyde, epichlorohydrin, and also unreacted monomers [4]. Plastic-based food contact materials may contain heavy metals that are either intentionally added as active ingredients during complex manufacturing processes using petrochemicals or generated as byproducts, impurities, or degradation products. These heavy metals may also be introduced through the recycling process of plastics [5,6]. It is common for individuals to come into contact with hazardous substances that can migrate from packaging materials into food during consumption [7]. European legislation (EU, 10/2011) establishes quality standards for food contact packaging materials and emphasizes that the materials used for food must not pose a risk to human health [8].

The analysis of migratory chemicals in real food products can be a time-consuming, expensive, and challenging process for sample preparation due to the complex composition of the food matrix. Consequently, migration studies often utilize food simulants instead of actual food [9]. Two elements are essential for conducting a migration experiment: the migration contact step, in which a food simulant is used to come into contact with the material, and the second step, which involves analytical measurement of the concentration of the analyte in the food simulant [8]. This migratory phenomenon occurs in three stages: migrant diffusion, dissolution and dispersion, and diffusion into food. However, the migrants into food are too diverse and the toxicity level variation makes the issue more complex [8,10]. Hence, the measurement of the inertness of a material is the overall migration limit and intentionally added monomers or additives must not be exceeded for the specific migration limits. Different national and international standards set specific migration limits (SML) and restriction conditions for some substances on the positive list [8,11]. These standards also establish a maximum limit of 60 mg/kg for overall migration (OML) from packaging materials into food. Additionally, the standards outline the requirements for compliance testing, which include the use of food simulants, specific migration test durations, and temperatures [8]. The variability in the quality of packaging materials produced by different manufacturers can result in different levels of heavy metal leaching. These hazardous materials may migrate into the food or beverages that people consume [12,13]. Furthermore, the leaching of heavy metals may also take place when numerous chemicals are present at different stages of the food supply chain. Heavy metals can enter the body through the consumption of food that contains migrated heavy metals, and these metals can accumulate in the body over time. This accumulation can disrupt the proper functioning of biological systems, potentially leading to diseases, even at low concentrations [14,15]. Arsenic (As), antimony (Sb), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), mercury (Hg), nickel (Ni),

Table 1
Description of food packaging materials based on polymer type.

S. N	Polymer type	Recycling Code No.	Description of sample	Name
1	Polyethylene Terephthalate (PET)	1	Drinking water bottle	PET-1
		1	Soft drinks bottle	PET-2
		1	Fruit juice bottle	PET-3
		1	Vegetable oil bottle	PET-4
		1	Biscuit box	PET-5
2	Polyethylene (PE)	2	Milk packet	PE-1
		2	Juice packet	PE-2
		2	Food carrying bag	PE-3
		2	Food wrapper (Transparent)	PE-4
		2	Food wrapper (PE Aluminium foil)	PE-5
3	Polypropylene (PP)	5	Ketchup packet	PP-1
		5	Lolly packet	PP-2
		5	Yogurt container	PP-3
		5	Coffee cup (Transparent)	PP-4
		5	Ice-cream box	PP-5
4	Polystyrene (PS)	6	Food carrying box	PS-1
		6	Onetime used plates	PS-2
		6	Onetime used cutlery	PS-3
		6	Food carrying cups	PS-4
		6	Plastic cup (White)	PS-5
5	Polycarbonate (PC)	7	Water pot	PC-1
		7	Refillable Water bottle	PC-2
		7	Refillable Water Jar	PC-3
		7	Baby water jar	PC-4
		7	Baby food jar	PC-5

and zinc (Zn) are the most common heavy metals potentially hazardous to human health [16].

Several carcinogenic and noncarcinogenic diseases, including cancer, intestinal disorders, tremors, diarrhea, hemoglobinuria, stomatitis, convulsions, depression, disruption of metabolic activity, and poor fetal development, may occur due to heavy metal exposure above the safety limit [16].

Also, various chronic diseases result from the consumption of such foods containing harmful chemicals [5]. A previous study by Ahmed et al. (2020) assessed the potential health risks among plastic industry workers of different ages in Bangladesh who had high levels of heavy metals such as Pb, Cd, and Ni in their blood [17]. Kiyataka et al. (2014) reported the presence of Pb (366.1–462.4 mg/kg) in yogurt cups made of high-density polyethylene that exceeded the safety limit recommended by the EU (2011) [18]. In another study, Whitt et al. (2012) found that the average Cd, Cr, Ni, and Pb concentrations in 29 recycled food packages made of PET were 8.82, 6.76, 9.43, and 0.15 mg/kg, respectively [2]. However, there is still limited information on the levels of heavy metals in PPMs and their potential health effects in Bangladesh.

Therefore, this study focuses on the overall migration of chemicals and heavy metals into food from the commonly used PPMs in Bangladesh. In this study, we aimed to characterize the plastic polymers and quantify the amount of heavy metals (Pb, Cd, Cr, Hg, Sb) leased out from the PPMs, which evaluate their compliance with the limits imposed by the legislation in force and to assess the health risks in Bangladesh.

2. Materials and methods

2.1. Sample collection and preparation

Several types of food packages made of plastic were collected from local markets in Bangladesh. After conducting FTIR analysis, we selected only twenty-five samples and categorized based on the polymer types for the present study: Polyethylene Terephthalate (PET), Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), and Polycarbonate (PC) **(Table 1).** Each category included five different types of samples based on their intended use. These samples were processed in the laboratory and studied for heavy metal migration. Furthermore, sample collection was accomplished considering their intended usage to identify potential risks to human health. Samples were tested six times repeatedly and triplicated when the observed values were not close. The entire research design of the study is illustrated in Fig. 1.

2.2. Chemicals and reagents

Nitric acid (HNO_3, 65%) and Hydrochloric acid (HCl, 37%) were purchased from Merck, Germany to prepare heavy metal standards. Calibration curves were obtained using a standard solution of 1000 mg/L of Pb, Cd, Cr, Hg, and Sb. All of the standards were purchased from Sigma Aldrich. Dilutions were performed using ultrapure water (18.2 MΩ cm). While for the overall migration test, Acetic acid (CH_3COOH, 100%) and Ethanol (C_2H_5OH, 99%) were purchased from Merck, Germany. All the glassware was soaked in 10% Nitric acid solution and kept overnight to remove trace metals and other impurities.

2.3. Identification of plastic

Plastics types of the collected samples were identified by the attenuated total reflectance fourier transform infrared (ATR-FTIR)

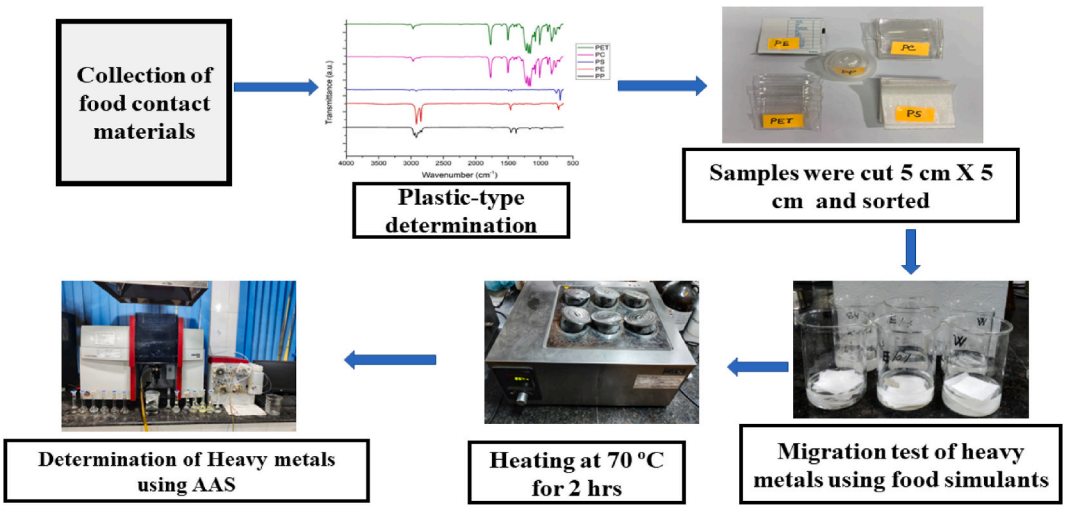


Fig. 1. Determination of migrated heavy metals from food-contact materials.

spectroscopy (Frontier, PerkinElmer, UK; Software: Spectrum version 10.4.4). Initially, the collected samples were washed with distilled water to remove dust particles and organic matter from the samples, then dried in an oven at 105 °C. The FTIR spectra were collected in attenuated total reflectance (ATR) mode equipped with a diamond crystal. The diamond crystal was cleaned with acetone for every measurement and a background scan was taken. The spectrum was recorded between 650 and 4000 cm^{-1} range at 4 cm^{-1} spectral resolution and 16 scans.

2.4. Overall migration test

The overall migration test was performed by using three different simulating solvents, including distilled water, 3% v/v CH_3COOH, and 15% v/v C_2H_5OH. For this analysis, samples were cut into pieces measuring 5 cm × 5 cm. The cut samples were placed in an oven at 105 °C for 4 h to eliminate moisture, and the weight of the dried samples was measured. Afterward, each type of polymer was placed in a separate beaker and immersed properly in 150 mL of experimental simulants. Then immersed samples were placed in a water bath at 70 °C for 2 h [8]. After the migration test, the plastic samples were taken out from simulants and dried in an oven at 105 °C for 4 h. The overall migration values were calculated by comparing the weight loss of the dried samples to their initial weights. A control experiment was conducted at the same time using three food-simulants without a sample. All the migration experiments were conducted in triplicate. The overall migration values were calculated using the following formula:

$$\text{Amount of migrated chemicals (mg / kg)} = \frac{\text{weight loss from plastic sample (mg)}}{\text{Total area of sample taken for migration } (dm^2)} \times 6\ dm^2$$

Where, 6 dm^2 surface area of plastic packaging was considered to come into contact with 1 kg of foods or simulants [19].

2.5. Determination of heavy metal contents

Standard solutions were prepared for the studied heavy metals (Pb, Cd, Cr, Hg, and Sb). The calibration curve for each element was performed using standard solution, with five calibration points utilized for each curve. The correlation coefficient of each calibration curve was higher than 0.995. The concentration of migrated Pb, Cd, Hg, Cr, and Sb in the distilled water simulant were analyzed by using Atomic Absorption Spectrophotometer (Analytikjena novAA, Germany) with acetylene gas. The instrument was calibrated using a standard solution prepared from the stock solution provided by Sigma Aldrich. The concentration of metals (in mg/kg) was calculated in the studied polymer samples.

2.6. Statistical analysis

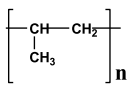
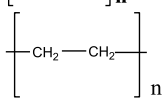
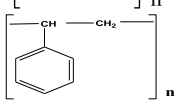
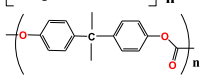
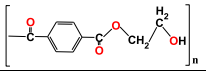
Statistical analysis was performed using Excel software (version 13). The data were presented as the mean ± standard deviation of triplicate values for each sample and its corresponding control solution. The level of significance was assessed by applying one-way analysis of variance (ANOVA) using Minitab 17 software. The p-value <0.05 was considered statistically significant.

3. Results and discussion

3.1. Identification of food contact materials

ATR-FTIR spectroscopy is one of the most important analytical techniques for the chemical characterization of polymers. The

Table 2
Characteristic absorption peaks obtained from the ATR-FTIR spectra of the polymers PP, PE, PS, PC, and PET samples were used for identification.

Polymer type	Structural unit	Characteristic absorption peaks (cm^{-1}) obtained from polymer used for identification
Polypropylene (PP)		2957, 2921, 2882, 2835, 1458, 1373, 1172, 980, 840
Polyethylene (PE)		2912, 2852, 1457, 1390, 722
Polystyrene (PS)		3059, 3022, 2934, 2852, 1600, 1498, 1453, 1023, 903, 758, 692
Polycarbonate (PC)		3040, 2970, 2930, 2873, 1776, 1598, 1406, 1229, 1192, 1153, 1082, 1007, 830
Polyethylene terephthalate (PET)		3065, 2961, 2924, 2860, 1712, 1623, 1571, 1506, 1405, 1234, 1088, 1012, 880, 718

characteristic absorption bands are utilized for identifying the polymer materials. In this study, 5 samples of each polymer type were used. The structural units and the primary absorption bands for each type of polymer are presented in Table 2. The spectra illustrated in Fig. 2 show the results obtained from the studied polymer samples.

Fig. 2a shows the characteristic absorption peaks at 2957, 2921, 2882, 2835, 1458, 1373, 1172, 980, 840 cm^{-1}, which are associated with the structure of PP. The absorption bands at 2957 and 2882 cm^{-1} are attributed to $–CH_3$ asymmetric, 2921 and 2835 cm^{-1} are attributed to $–CH_2$ symmetric stretching vibrations, respectively. The peaks at 1458 and 1373 cm^{-1} indicate the presence of $–CH_2$ and $–CH_3$ bending vibrations, respectively. The bands at 1172 cm^{-1} are due to the presence of C–C stretching vibration. The $–CH_3$ rocking and C–C stretching vibration was observed at 980 cm^{-1}, $–CH_2$ rocking and C–CH_3 stretching at 840 cm^{-1}. Different authors observed Similar results for the PP polymer [20–22].

Fig. 2b shows several characteristic absorption bands obtained from PE samples: CH_2 asymmetric and symmetric stretching vibration at 2912 cm^{-1} and 2852 cm^{-1}. Jung et al., 2018 observed $–CH_2$ asymmetric and symmetric stretching vibration at 2915 cm^{-1} and 2845 for low-density polyethylene polymer [21]. $–CH_2$ bending at 1457 cm^{-1}, $–CH_2$ symmetric deformation, and $–CH_2$ rocking vibration at 722 cm^{-1} was observed. Thus, the obtained characteristic absorption bands from the FTIR spectra confirm the polymer PE. The spectrum in Fig. 2c shows various absorption peaks found from FTIR related to the structure of PS. The absorption bands at 3059 cm^{-1} and 3022 cm^{-1} (C–H stretching vibration in the aromatic ring), 2934 cm^{-1} and 2852 cm^{-1} ($–CH_2–$ asymmetric and symmetric stretching vibrations), 1600 cm^{-1} and 1498 cm^{-1} (aromatic ring stretched), 1453 cm^{-1} ($–CH_2$ bending), 1023 cm^{-1} (aromatic C–H bending), 903 cm^{-1}, 758 cm^{-1} and 692 cm^{-1} (aromatic C–H out of plane bending) [20,21].

Functional groups and their characteristic absorption peaks for the PC samples were investigated and tabulated in Table 2. Again, Fig. 2d shows different absorption peaks at 3040, 2970, 2930, 2873, 1776, 1598, 1406, 1229, 1192, 1153, 1082, 1007, and 830 cm^{-1}, which are connected to the structure of PC. Some other authors also found similar properties of PC in different studies [20–22].

The peak at 3040 cm^{-1} is due to the C–H stretching vibration in the aromatic ring. The absorption peaks at 2970 cm^{-1}, 2930 cm^{-1},

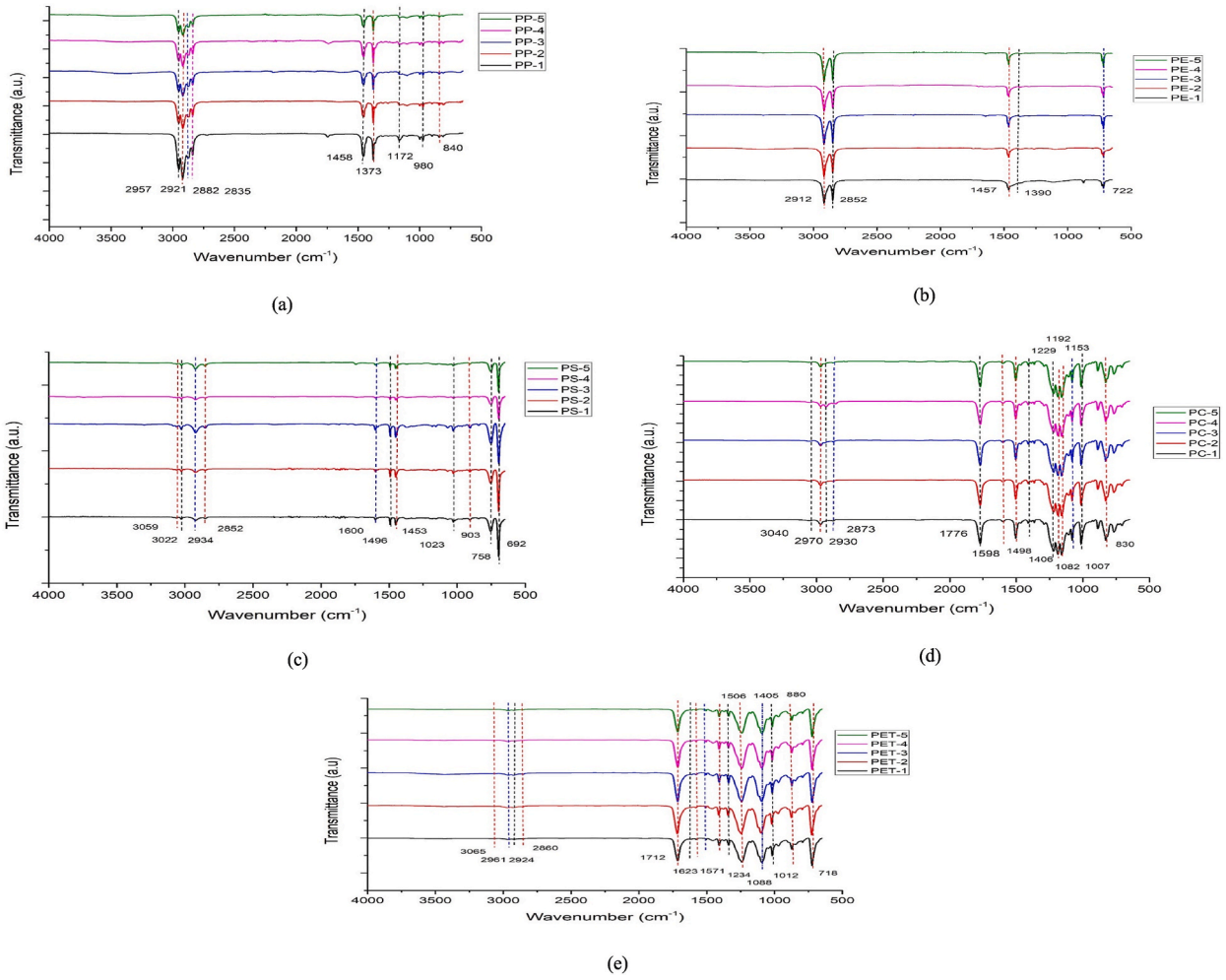


Fig. 2. Comparison of ATR-FTIR spectra of the 25 selected samples and their categorization: (a) polypropylene (PP), (b) polyethylene (PE), (c) polystyrene (PS), (d) polycarbonate (PC), and (e) polyethylene terephthalate (PET).

and 2860 cm^{-1} are ascribed to C–H stretching vibrations in alkyl groups. The absorption peak at 1776 cm^{-1} is corresponding to C═O stretching vibration. The band at 1598 cm^{-1} is a result of C═C stretching vibration in the aromatic ring. Peaks at 1406 cm^{-1},1229 cm^{-1} indicate the presence of C–H (–CH_3) asymmetric and symmetric vibration in the plane. The peaks at 1192 cm^{-1} and 1153 $cm^{-1}$are due to the C–O stretching vibration. The peak at 1082 cm^{-1} is due to C–H stretching in the aromatic ring. The bands at 1007 cm^{-1} and 830 cm^{-1} are due to aromatic C–H in and out of the plane, respectively. These characteristic absorption bands confirm the studied sample was PC.

ATR-FTIR spectra of PET samples (Fig. 2e) studied in this research show several absorption bands depending on the functional groups are presented in Table 2. The characteristic band at 3065 cm^{-1} is clearly observed for PET samples. These bands correspond to the –C–H stretching in the aromatic ring. The bands at 2961 cm^{-1}, 2924 cm^{-1}, and 2860 cm^{-1} are attributed to the –C–H stretching vibrations. The sharp peak at 1712 cm^{-1} confirms C═O stretching vibration in the ester group. Asensio et al. (2009) found the same C═O stretching vibration for the ester group in the PET sample [20], which differentiated PET and PC samples from PP, PE, and PS polymer (Fig. 2). The bands at 1623 cm^{-1}, 1571 cm^{-1}, and 1506 cm^{-1} indicating C═C stretching an aromatic ring. The peak at 1405 cm^{-1} is due to C–H stretching in the aromatic ring.1234 cm^{-1} is due to C–O stretching vibration. The bands at 1012,1008 and 880 cm^{-1} are due to the aromatic ring. The peak at 718 cm^{-1} is attributed to C–H aromatic ring wagging vibration.

3.2. Heavy metal standards

Globally, heavy metal migration from plastic-based food contact materials into food is becoming a major public health concern. Many countries and food safety organizations have established standards and safety limits for migrating heavy metals from food contact materials into foods [8,23,24]. The amount of heavy metal (Pb, Cd, Cr, Hg, and Sb) migrated from the food contact material is needed to measure. However, there is no specific standard for heavy metal content in food contact material, though a large volume of plastic packaging material is globally used daily. Therefore, heavy metal content migrated from plastic packaging material can be compared with the allowable specific migration limit, overall migration limit, and acceptable heavy metal content in drinking water **(Table 3).**

3.3. Overall migration test

Overall migration test was carried out under standardized test conditions, including testing time, temperature, and test medium (food simulant) representing the worst possible conditions of use of the plastic material, to achieve comparable results in the verification of compliance with the overall migration limit (OML). In this study, migration at 70 °C for 2 h was chosen to represent the worst foreseeable conditions of using plastic food contact material by following the EU legislation [8,27]. Chemicals were migrated from all samples and found to contain varying concentrations ranging from (0.27 ± 0.06) to (3.50 ± 0.17) mg/kg in distilled water, (0.33 ± 0.06) to (9.17 ± 0.15) mg/kg in 3% acetic acid, and (0.37 ± 0.12) to (7.37 ± 0.15) mg/kg in 15% ethanol **(Table 4).** In the case of the water simulant, the PP-4 sample (coffee cup) exhibited the highest overall migration. PE-5 (food wrapper) and PP-3 (yogurt container) were also found to release a significantly higher amount of chemicals ($p < 0.05$) in water during the migration test. Overall migration was highest in the PP-3 sample for both 3% acetic acid and 15% ethanol **(Table 4).**

It was also noticed that the migrating behaviors of chemicals from food contact materials depend on simulants. All the samples demonstrated migrating behavior less than the standard allowable overall migration limits **(Table 3).** According to BDS 1976:2020 and EU Regulation no 10/2011, the maximum OML for plastic food contact materials was 60 mg/kg [8,11].

3.4. Migration of heavy metals into simulants

Fig. 3a represents the amount of Pb that migrated into the water simulant after being exposed to 70 °C for 2 h. The highest migration of Pb was observed in sample PP-2, while the lowest was observed in PS-2. The amount of Pb migration was similar in the cases of PP-2, PE-1, PS-4, and PS-5. Comparatively lower Pb migration was found in PET and PC samples. Pb migration was within the safe limits for all samples, as per the permissible limits set by EU regulation [8] and BDS 1976:2020 [11]. It exceeds the safety limit for Pb content in drinking water recommended by the WHO (0.01 mg/L) [23]. These results were also higher than the maximum allowable

Table 3
Maximum allowable limits for heavy metals according to European union regulation (EU) no. 10/2011, Bangladesh *Standards* (BDS) 2020, world health organization (WHO), health Canada, and Bureau of Indian Standards (BIS).

Standards	Overall migration limit	Specific migration of heavy metals					Ref.
		Pb	Cd	Hg	Cr	Sb	
Plastic food contact material (mg/kg)							
EU no. October 2011	60.0	2.0	–	–	1.0	<0.04	[8]
BDS 1976:2020	60.0	2.0	2.0	2.0	–	–	[11,23]
Allowable maximum limit of heavy metals in drinking water (mg/L)							
WHO	–	0.01	0.003	0.006	0.05	0.02	[23]
Health Canada	–	0.005	0.005	0.001	0.05	0.006	[25]
BIS (10500: 2012)	–	0.01	0.003	0.001	0.05	–	[26]

Table 4
Simulants influenced migrating chemicals (mg/Kg) at 70 °C for 2h

Polymer type	Migration of chemicals from samples (mg/kg)		
	Distilled water	3% Acetic acid	15% Ethanol
PET-1	1.47 ± 0.06^{cd}	1.57 ± 0.12^{ef}	1.93 ± 0.15^{efgh}
PET-2	2.47 ± 0.06^{b}	2.86 ± 0.21^{c}	2.87 ± 0.15^{cd}
PET-3	0.56 ± 0.06^{g}	0.80 ± 0.10^{hij}	0.53 ± 0.12^{jk}
PET-4	2.43 ± 0.06^{b}	3.20 ± 0.17^{c}	2.47 ± 0.12^{cde}
PET-5	0.97 ± 0.21^{f}	1.23 ± 0.06^{fgh}	1.33 ± 0.12^{ghi}
PP-1	0.57 ± 0.06^{g}	0.37 ± 0.12^{j}	0.40 ± 0.10^{k}
PP-2	1.00 ± 0.1^{ef}	0.40 ± 0.10^{j}	0.57 ± 0.06^{jk}
PP-3	3.26 ± 0.06^{a}	9.17 ± 0.15^{a}	7.37 ± 0.15^{a}
PP-4	3.50 ± 0.17^{a}	3.86 ± 0.06^{b}	4.27 ± 0.12^{b}
PP-5	0.27 ± 0.06^{g}	0.50 ± 0.10^{ij}	0.50 ± 0.10^{k}
PE-1	0.93 ± 0.15^{f}	0.63 ± 0.06^{ij}	1.73 ± 0.72^{fgh}
PE-2	0.33 ± 0.06^{g}	0.53 ± 0.12^{ij}	0.37 ± 0.12^{k}
PE-3	1.56 ± 0.06^{c}	1.67 ± 0.67^{def}	2.23 ± 0.15^{def}
PE-4	0.57 ± 0.06^{g}	0.33 ± 0.06^{j}	0.37 ± 0.12^{k}
PE-5	3.40 ± 0.17^{a}	0.57 ± 0.06^{ij}	0.80 ± 0.10^{ijk}
PC-1	1.23 ± 0.06^{def}	1.23 ± 0.06^{fgh}	1.23 ± 0.06^{hij}
PC-2	2.20 ± 0.10^{b}	2.00 ± 0.20^{de}	1.90 ± 0.10^{efgh}
PC-3	0.40 ± 0.10^{g}	0.43 ± 0.15^{j}	0.53 ± 0.12^{jk}
PC-4	1.57 ± 0.06^{c}	2.13 ± 0.15^{d}	1.97 ± 0.15^{efg}
PC-5	2.33 ± 0.12^{b}	1.83 ± 0.06^{de}	3.10 ± 0.10^{c}
PS-1	0.27 ± 0.06^{g}	1.00 ± 0.10^{ghi}	0.53 ± 0.12^{jk}
PS-2	1.50 ± 0.10^{cd}	1.23 ± 0.06^{fgh}	1.23 ± 0.67^{hij}
PS-3	2.40 ± 0.10^{b}	1.57 ± 0.12^{ef}	1.73 ± 0.12^{fgh}
PS-4	1.30 ± 0.10^{cde}	1.50 ± 0.10^{efg}	0.43 ± 0.15^{k}
PS-5	2.20 ± 0.10^{b}	1.23 ± 0.06^{fgh}	1.63 ± 0.06^{fgh}

*Use of different superscripts within the samples in the same column indicates significant differences in the concentrations ($p < 0.05$).

concentration of Pd in fruits and vegetables, which ranges from 0.05 to 0.3 mg/kg, 0.2 mg/kg in cereal grains, and 0.3 mg/kg in fish [8]. Pb is classified as a carcinogen by the International Agency for Research on Cancer (IARC) and is placed in Group 2A [28]. Excessive exposure to lead (Pb) can result in various adverse health effects, including hypertension, gastrointestinal problems, stunted growth, nervous system dysfunction, cognitive disabilities, hearing loss, and reproductive issues [16].

Cd migration (0.36 ± 0.01 mg/kg) was found to be maximum in the PP-2 sample (lolly packet). PP-2, PP-1, PP-5, and PS-5 samples released a significantly higher amount of Cd, while all the PET, PE, and PC samples had lower Cd values (Fig. 3b). The level of Cd migration from all plastic samples into the water was lower than the acceptable limit recommended by BDS 1976:2020 [11]. However, the level of Cd migration from all plastic samples exceeded the recommended acceptable limit of Cd in drinking water (0.003 mg/L) and in fruits and vegetables (0.05–0.1 mg/kg) of FAO/WHO [29]. Cd accumulates in the human body, particularly in the kidneys, and can cause kidney damage [30].

Hg migration was higher in the case of polycarbonate samples and maximum in the PC-5 sample (0.27 ± 0.01 mg/kg) (Fig. 3c). Hg concentration in drinking water should not exceed the limits set by several organizations, including BDS (2 mg/kg) for plastic, WHO (0.003 mg/L), Health Canada (0.001 mg/L), and BIS (0.001 mg/L) **(Table 3).** The result revealed that the level of Hg migration from all the plastic samples into the water was lower than the acceptable limit recommended by BDS 1976:2020. The finding of this study revealed that the amount of Hg leached from the samples was not within acceptable limits.

The concentration of migrated Cr (0.12 ± 0.01 mg/kg) was significantly higher in sample PET-2, which corresponds to soft drink bottles (Fig. 3d). The concentration of Cr ranged as follows: PET samples (0.06 ± 0.01 to 0.12 ± 0.01) mg/kg, PP samples (0.05 ± 0.01 to 0.08 ± 0.01) mg/kg, PE samples (0.05 ± 0.01 to 0.07 ± 0.01) mg/kg, PC samples (0.05 ± 0.01 to 0.07 ± 0.02) mg/kg, and PS samples (0.06 ± 0.02 to 0.08 ± 0.01) mg/kg. The migration of heavy metals from all samples is within the permissible limit recommended by EU Regulation October 2011 [8]. The maximum allowable limit of Cr in fruits and vegetables is 2.3 mg/kg [29]. Unfortunately, the amount of Cr migrated from all the samples exceeded the permissible limit of this metal in drinking water, which is 0.05 mg/L [23,25,26].

Unfortunately, Sb migration from all the samples was very alarming as it exceeded the allowable limit (<0.04 mg/kg) set by EU Regulation October 2011 [8]. The concentration of Sb in water simulant varied as follows: PET samples (0.05 ± 0.02 to 0.09 ± 0.01) mg/kg, PP samples (0.05 ± 0.01 to 0.08 ± 0.01) mg/kg, PE samples (0.05 ± 0.01 to 0.08 ± 0.01) mg/kg, PC samples (0.05 ± 0.01 to 0.07 ± 0.01) mg/kg, and PS samples (0.05 ± 0.01 to 0.08 ± 0.01) mg/kg, as shown in Fig. 3e. The World Health Organization (WHO) recommends that the concentration of Sb in drinking water should not exceed 0.02 mg/L [23].

Heavy metal exposure through consuming contaminated food is a common pathway that can lead to various diseases in humans when it exceeds the recommended limit [16]. All of the samples were found to release heavy metals in hot water at 70 °C temperature (Fig. 3). Migration occurs due to factors such as high food temperatures, storage duration, and production processes. The higher the temperature, the greater the likelihood of migration [31]. According to BDS 1976:2020, the migration of Pb, Cd, and Hg should not exceed 2 mg/kg. Additionally, EU Regulation October 2011 specifies that the Cr content should not exceed 1 mg/kg and the Sb content should be less than 0.04 mg/kg (Table 2). In the production of polymers such as PE, PP, PS, PET, and PC, various catalysts are used that

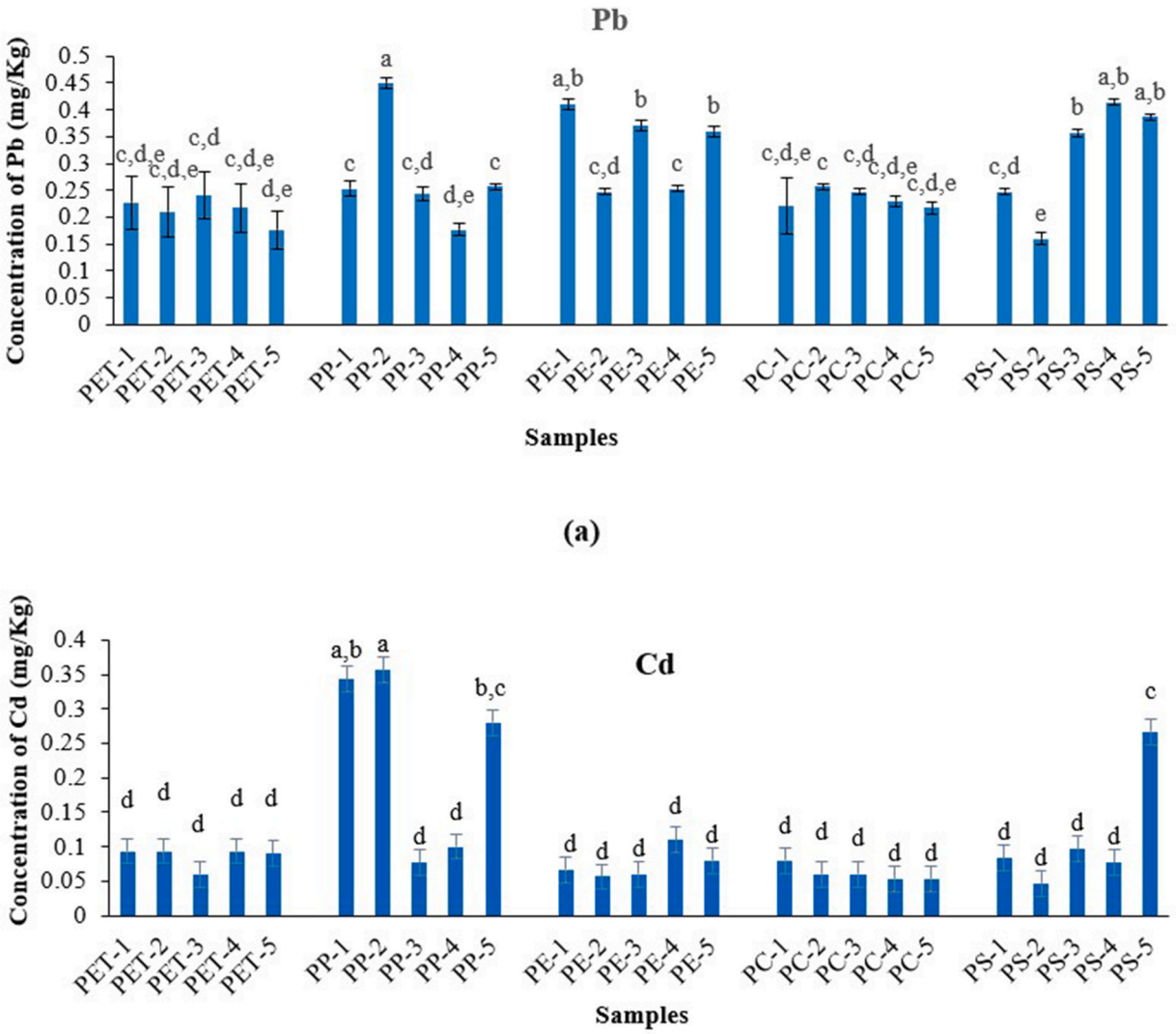
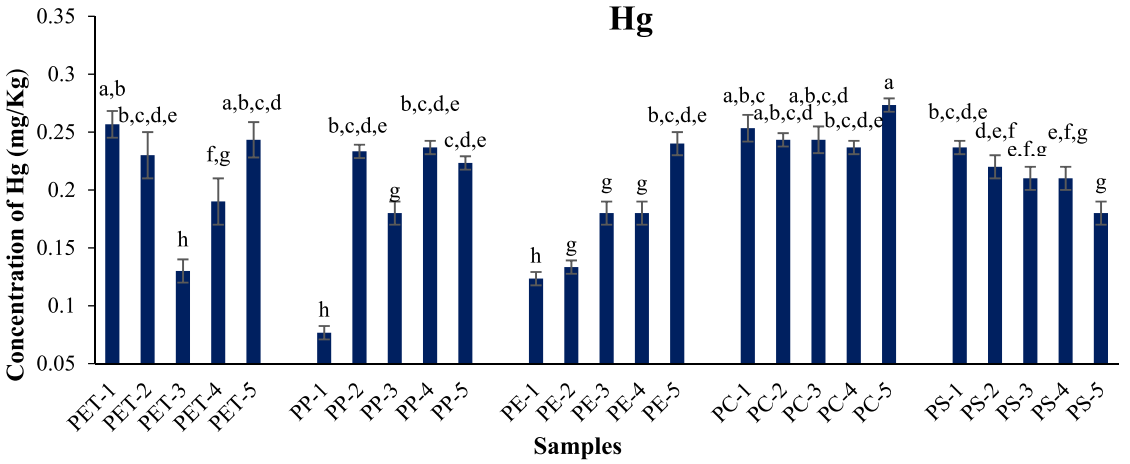


Fig. 3. The concentration of heavy metals (Pb, Cd, Hg, Cr, and Sb) in plastic samples. The use of different superscripts within the samples indicates significant differences in the concentrations ($p < 0.05$).

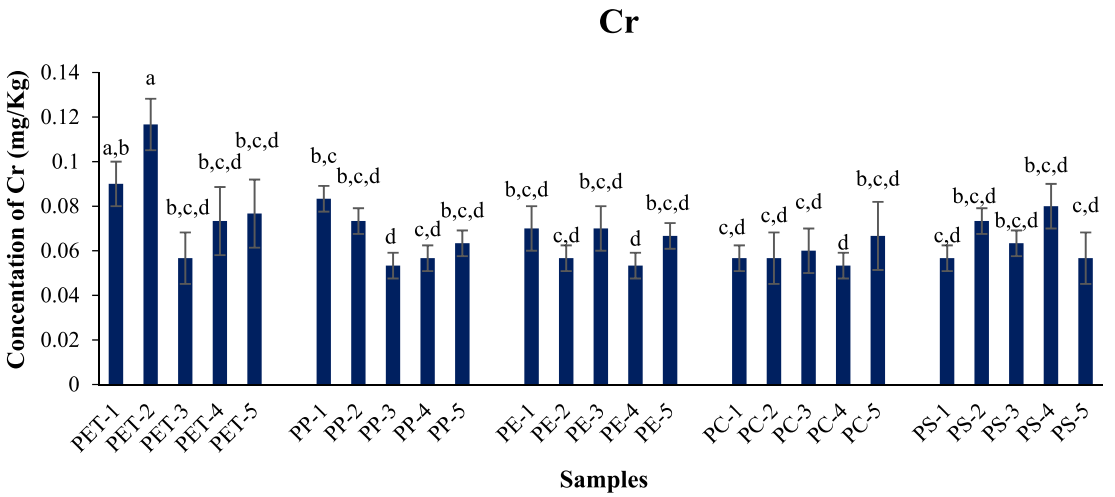
may contain low levels of heavy metals. Generally, plastics used for food packaging may also contain these metals in the form of additives, such as pigments and stabilizers. The quantification of heavy metals is crucial because they have the potential to contaminate food and cause toxicity [26]. According to Article 3(1)(b) of Regulation (EC) No. 1935/2004, the release of substances from food contact materials and articles should not cause any unacceptable changes in the composition of the food. According to good manufacturing practices, it is possible to produce plastic materials in a manner that limits the release of substances to no more than 10 mg per 1 dm^2 of the plastic material's surface area [8].

4. Limitations of the study

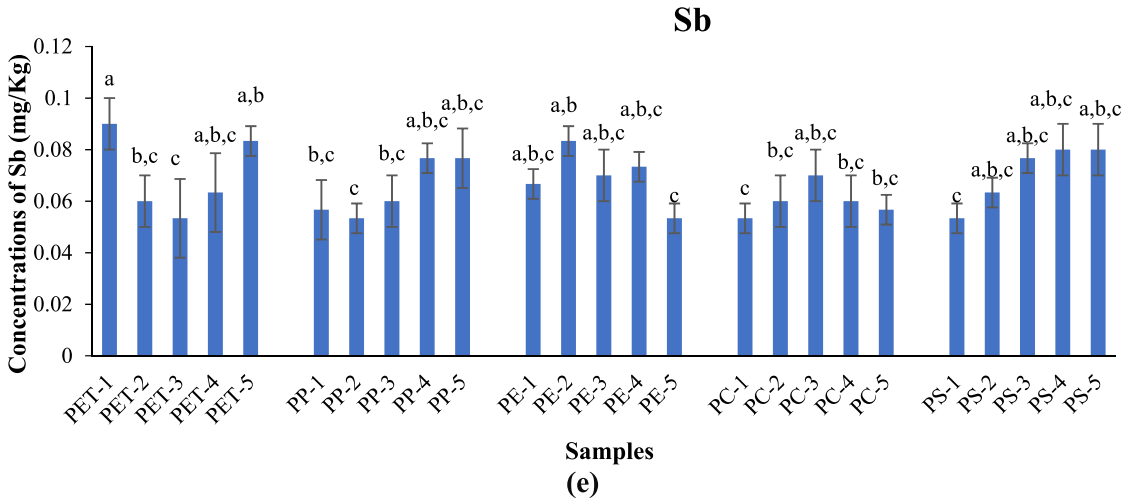
To the best of our knowledge, this is the first study on the migration of heavy metals from plastic food contact materials in Bangladesh. However, the study has certain limitations. This study involved identifying the polymer and quantifying heavy metal migration from these materials but didn't include the heavy metal content of plastic samples. Again, only 25 samples were tested for heavy metal migration, which may not provide a comprehensive representation of the heavy metal migration status of all food packages used in Bangladesh. Moreover, this study only analyzed five heavy metals using only distilled water as a food simulant recommended by Commission Regulation (EU) No. October 2011 [8]. However, the migration of heavy metals may not be precisely predicted by using food simulants instead of real food [32].



(c)



(d)



(e)

Fig. 3. (*continued*).

5. Conclusion

Hazardous materials in food-contact plastic packages have recently raised public safety and health concerns. The Results revealed that all the samples migrated heavy metals, including Pb, Cd, Hg, Cr, and Sb, in hot water. The obtained results were compared with maximum allowed limits stated by the legislation in force: EU no. 10/2011, BDS1976:2020, WHO, Health Canada, and BIS (10500: 2012). Migration of Pb, Cd, Hg, and Cr from all the samples is within the permissible limit recommended by the EU Regulation October 2011 and BDS 1976:2020 for plastic. Whereas all the samples leached Sb higher than the maximum allowed limits as declared by the EU regulation no. October 2011. This study enhances the understanding of the leaching of heavy metals from widely used polymers such as PET, PE, PP, PS, and PC, in Bangladesh. The findings of this study may also be useful in developing risk management strategies. At the same time, this assessment will be helpful for the manufacturers to ensure the quality of FCMs in Bangladesh and other countries. Future studies can be carried out to assess the heavy metal migration in case of real food and public health risks under consumption.

Author contribution statement

Shamima Akther Eti: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper. **Muhammad Saiful Islam:** Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data. **Jahid Hasan Shourove:** Conceived and designed the experiments, Analyzed and interpreted the data; Wrote the paper. **Badhan Saha:** Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data. **Swapan Kumer Ray:** Conceived and designed the experiments; Analyzed and interpreted the data. **Shahin Sultana:** Conceived and designed the experiments, Contributed reagents, materials, analysis tools or data. **Md. Aftab Ali Shaikh:** Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data. **Mohammad Mahbubur Rahman:** Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare no conflict of interest.

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