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Risk of human exposure to metals in some household hygienic products in Nigeria

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ABSTRACT

This study presents data on the levels and risk of human exposure to Cd, Pb, Cr, Ni, Cu, Co, Mn, Zn and Fe in some popular brands of household hygienic products (HHPs) available in Nigeria. The HHPs were digested with a mixture of HNO_3, HCl and $HClO_4$ in a ratio of 1:3:1 and the concentrations of the selected metals were quantified by atomic absorption spectrophotometry. The metal concentrations (in μg g^{-1}) in these products ranged from 0.4 to 5.4, < 0.09–47.0, < 0.12–43.7, < 0.06–7.5, < 0.12–9.5, < 0.06–15.0, < 0.09–24.5, 9.0–675 and 62.4–434 for Cd, Pb, Cr, Cu, Co, Ni, Mn, Zn and Fe respectively. The systemic exposure dosages for the metals, arising from the use of these HPPs, were less than their respective provisional tolerable daily intake/recommended dietary allowance values. The household hygienic products are safe to use by humans based on the margin of safety values that were all above 100. However, the products contained significant levels of toxic (Cd and Pb), allergenic (Ni and Cr) and other low toxicity metals (Mn, Zn and Fe), which could be a potential threat to the environment.

1. Introduction

The metallic content of household detergents, soaps and cleansing products is of environmental and health concern for a number of principal reasons. These include: (i) the direct exposure of humans to these metallic contaminants in soaps during washing, (ii) ingestion of these contaminants from improperly rinsed household utensils like cups and plates, amongst others, (iii) effluents from washing processes that are discharged directly into the environment without treatment, which may increase the contaminant burden of the environment, and (iv) metals that may be transferred from soaps and detergents into fabrics, which may not be completely removed by rinsing, and therefore constitute an indirect exposure route of these contaminants in detergents and soaps.

Detergents and soaps are indispensable cleansing products that form part of our daily routines in homes, offices, schools, hospitals, restaurants, etc. They play an important role in removing dirt, germs and other contaminants, and thus promote a hygienic lifestyle. Soap is a traditional washing product produced from the saponification of oil with alkali. A wide variety of fats and oils have been used for soap production including tallow, lard, palm kernel oil, coconut oil, and marine oil, amongst others, in Nigeria. Currently, palm oil and palm kernel oil are the most widely used [1]. Household detergents and soaps are used in high volume and on a daily basis. In Nigeria, the annual national demand for soap is estimated at 4950 million bars, which implies a per capita consumption of 30 tablets per year considering the estimated human population of 165 million [1]. A wide variety of chemical substances have been used in household detergents and most of them have been officially classified with respect to their possible toxicity effects on humans, however, only a limited number of these chemical substances have been categorized on the basis of their possible adverse environmental effects [2–5]. The use of personal care and household hygienic products could be a possible source of daily exposure of humans to contaminants in these products [6–8]. However, the impact of this continual exposure and the cumulative interactions on health risk assessment are poorly understood [7].

Although some metals can be categorised as potentially toxic (e.g. Cd and Pb), others are probably essential (e.g. Co and V) or essential

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(e.g. Cu, Zn, Fe, Mn) [9]. Nevertheless, exposure to metals can be responsible for a wide variety of disorders in humans including behavioural disorders, deficiencies in learning and hearing, irreversible neurological impairment, cancer, allergic contact dermatitis (ACD), endocrine disruption, respiratory problems, and reproductive, hepatic and renal system dysfunction [10–12]. Knowledge of the concentrations of metals in detergents and soaps would enable the consumers to make choices based on the safety of the products and, also, assist the manufacturers of these products to control the processes that could lead to high levels of these metals in the finished products. Therefore, this study sought to quantify the levels of nine metals in a range of frequently used household detergents and soaps available in Nigeria and to evaluate the likely risk through use of these products as estimated by the systemic exposure dosages (SEDs) and margin of safety (MoS) values derived from the metal concentrations measured.

2. Materials and methods

2.1. Samples and sample collection

In this study, samples of 27 brands of HHPs, comprising of ten brands of powdered detergents, eight brands of bar soaps, three brands of liquid soaps used for dish washing, and two brands each of hand sanitizers, spot removers and hand creams, were bought from different sale outlets in Abraka, Sapele and Warri in Delta State, Nigeria. For each brand of household product, three to five samples with different dates of manufacture and batch numbers were purchased in order to evaluate the variation in metal concentrations within a particular product. The brands of HHPs studied were carefully chosen to reflect market popularity, pricing and those used by different income groups. Some characteristic information about each product, such as brand name, colour and country of origin, is provided in Table 1.

Table 1
Information on the household hygienic products investigated.

Brand	Sample code	Colour	Country of Origin
Household detergents			
Rana	HD1	White	Nigeria
Canoe	HD2	White	Nigeria
Klin	HD3	White	Nigeria
WAW	HD4	White	Nigeria
Sunlight	HD5	White	Nigeria
Good Mama	HD6	White	Nigeria
Omo	HD7	Blue	Nigeria
ZIP	HD8	White	Nigeria
MYMY	HD9	White	Nigeria
Ariel	HD10	White	Nigeria
Household liquid soaps			
Mama lemon	HLS11	Green	Nigeria
Morning fresh	HLS12	Green	Nigeria
Super shine	HLS13	Green	Nigeria
Household bar soaps			
Soda white	HBS14	White	Nigeria
Canoe extra care	HBS15	White	Nigeria
Soda blue	HBS16	Blue	Nigeria
WAW soap	HBS17	White	Nigeria
Klin soap	HBS18	White	Nigeria
B29 soap	HBS19	White	Indonesia
Canoe quality	HBS20	White	Nigeria
Black native soap	HBS21	Black	Nigeria
Hand sanitizers			
Rx sanitizer	HS22	Green	USA
Lachi gel	HS23	Colourless	Italy
Spot-removing creams			
Spot removing cream	SRC24	Brown	USA
Beauty magic	SRC25		
Hand/body creams			
Hand cream	HBC26	White	USA
DAX pomade	HBC27	Green	USA

2.2. Reagents

The acids used for the sample digestion were of analytical grade and included hydrochloric acid, HCl (37% v/v, BDH, Poole, United Kingdom), nitric acid, HNO_3 (69% v/v), and perchloric acid, $HClO_4$ (70% v/v, Rieldel-de Haën, Seelze, Germany). All solutions were prepared with deionised water obtained from a Millipore Elix UV5 water purification system (Millipore, USA). The working standards for the test metals were prepared in 0.25 mol L^{-1} HNO_3 by serial dilution of 1000 mg L^{-1} commercial standards.

2.3. Sample preparation and chemical analysis

A 0.5 g mass of each sample was measured into a 150 mL Teflon beaker, followed by the addition of 9 mL of HCl, 3 mL of HNO_3 and 3 mL of $HClO_4$. The sample was covered and allowed to pre-digest for at least 3–4 hours. Thereafter, the sample mixture was placed in a regulated heating block and heated to 110 °C for 1 h. The clear digest was cooled to room temperature; and the cover was rinsed into the digest with 0.25 mol L^{-1} HNO_3. The sample was passed through a Whatmann No. 1 filter paper and diluted with 0.25 mol L^{-1} HNO_3 to 25 mL [6]. The blanks (n = 3) were prepared in a similar manner but the sample was omitted. The sample solutions were analysed for Cd, Pb, Cr, Ni, Co, Cu, Fe, Mn and Zn by means of atomic absorption spectrophotometry (PerkinElmer Analyst 200, Norwalk, CT, USA). The blanks and calibration standards were analysed in the same manner as the samples.

2.4. Quality assurance/control

All glassware and sample containers were washed with metal-free detergent and soaked in 10% HNO_3 for 24 h. These items were subsequently rinsed with double-distilled and deionised water. Since there is no available certified reference material for these product types, a spike recovery method was adopted to validate the efficiency of the analytical method. The average percentage recoveries for Cd, Pb, Cr, Ni, Co, Cu, Mn, Zn and Fe, determined at three concentration levels, were 96.4, 84.9, 93.7, 92.2, 96.7, 88.9, 97.9, 94.7 and 101.8% respectively. The analysis of all samples was performed in triplicate with relative standard deviations ranging between 2 and 10%. The R^2 values of the calibration lines for the metals varied between 0.9995 and 0.9999. The limits of detection (LODs) and quantification (LOQ) were determined as the 3:1 and 10:1 signal-to-noise ratio of the blank respectively. The LODs for Cd, Pb, Cr, Ni, Cu, Co, Mn, Zn and Fe were 0.02, 0.03, 0.04, 0.02, 0.02, 0.04, 0.03, 0.04 and 0.03 respectively; while the LOQs were 0.06, 0.09, 0.12, 0.06, 0.06, 0.12, 0.09, 0.12 and 0.09 for Cd, Pb, Cr, Ni, Cu, Co, Mn, Zn and Fe respectively.

2.5. Statistical analysis

The significance of the intra- and inter-brand differences in the metal concentrations was evaluated by using analysis of variance (ANOVA), while the Tukey test was used to determine the significance of the differences in the elemental levels between the various categories of HHPs investigated. SPSS software version 24 (SPSS Inc., Illinois, USA) was used for all statistical analyses.

2.6. Evaluation of human exposure risk

The uncertainty factor termed “margin of safety” (MoS) was used to determine the likely risk to humans from exposure to metals in these HHPs. The MoS is obtained by normalizing “the lowest no-observed-adverse-effect-level (NOAEL) value of the metals” with their respective estimated systemic exposure dosage (SED) [13]:

$$MoS = \frac{NO(A)EL}{SED}$$

Table 2
Standard values of variables used in computing Systemic Exposure Dosage values [13].

Type of personal care product	Amount applied daily (AA)/g	Skin surface area (SSA)/cm^2	Frequency of application per day (F)	Retention factor (RF)
Detergent	20.0	860	2	0.01
Liquid soap	20.0	860	2	0.01
Bar soap	20.0	860	2	0.01
Hand sanitizer	20.0	860	10	0.01
Spot-removing cream	1.54	565	2.14	1
Hand/body cream	2.16	860	2	1

The SED was evaluated by using the equation:

$$SED\ (\mu g\ kg^{-1}\ bw\ day^{-1}) = \frac{Cs \times AA \times SSA \times F \times RF \times BF}{BW} \times 10^{-3}$$

where Cs denotes a particular metal concentration in the HHP (mg kg^{-1}); AA represents the amount of HHP used per day; SSA represents the skin surface area that is in contact with the product; F is the frequency of application; RF denotes the retention factor; BF denotes the bioaccessibility factor; the unit conversion factor is 10^{-3}; and BW represents the human body weight (which in this work was taken to be 60 kg).

The AA values for some of the different groups of HHPs were derived from their per capita consumption values and from the standard values established by the SCCS [13]. The average mass of a typical bar soap is 250 g. The values for AA, SSA, F and R applied in our study are listed in Table 2. In this study, the SCCS model equation was modified by the introduction of a dilution factor (DF) to account for the diluent effect of water during washing. We assumed a DF of 0.2, which implies that an average of 5 L of water is used to reconstitute the detergent or soap during washing. In the case of hand sanitizers, spot-removers and hand creams, the DF value used was 1 because they do not require the use of water for use. The NOAEL values of the metals were obtained by multiplying their oral reference doses (RfD) (defined as the daily amount of exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of harmful effects during a person's lifetime) with the uncertainty factors UF and MF (i.e. NOAEL = RfD × UF × MF). UF represents the uncertainty factor and has a default value of 100. It reflects the overall confidence in the various data sets and MF represents the modifying factor based on the scientific judgment used and has a default value of 1. The RfDs (in mg kg^{-1} day^{-1}) for the metals studied are Pb (4×10^{-3}) [10], Cd (1×10^{-3}), Cu (4.0×10^{-2}), Co (3×10^{-4}), Cr (3×10^{-3}), Fe (7.0×10^{-1}), Mn (1.4×10^{-1}), Ni (2×10^{-2}) and Zn (3.0×10^{-1}) [15]. The MoS value of 100 is set as the minimum acceptably safe level for a product that is used on human skin [13]. The SCCS has recognized the fact that when there is no oral absorption data available, 100% absorption of the administered substance is usually assumed in most MoS calculations. However, in calculating MoS values, it is more reasonable to assume that the systemic absorption of the administered dose does not exceed 50% [13]. Where there is indication of poor oral availability, e.g. poorly soluble particulates, 10% systemic availability of the administered dose is considered appropriate [13]. In this study, we assumed 50% (as the midpoint scenario) and 100% (as the worst-case scenario) systemic availability of the investigated metals in evaluating the safety of these HHPs.

3. Results and discussion

The concentrations of the nine metals measured in a selection of household hygienic products are given in Table 3. The concentrations showed significant dispersion ($p < 0.05$) from one brand to another and between the various groups. The diverse levels of metals in the HHPs may be related to differences in the raw materials used, and the branding and manufacturing processes [10,11,16].

The levels of Cd in the HHPs varied between 0.4 and 5.4 μg g^{-1}. The highest level of Cd was found in HD4. Cadmium concentrations in these HHPs were in the following order: detergents > bar soaps > liquid soaps > hand sanitizers > hand creams. The Cd concentrations in the HHPs fall within the limits specified by the Canadian and German authorities for Cd in cosmetics (3.0 μg g^{-1} and 5.0 μg g^{-1} respectively) except for sample HD4 [17,18]. The Cd concentrations in these samples are comparable to those found in household detergents from Kayseri, Turkey (1.7 to 2.8 μg g^{-1}) [5]. Abulude et al. [19] found the Cd levels in soaps and detergents from Western Nigeria to be lower than the detection limit of their spectrophotometric analysis technique. The absorption of Cd through the skin is controlled by complexation and induction with metallothionein, or interaction between free Cd ions and sulfhydryl radicals of cysteine present in epidermal keratins [20].

The Pb content in these brands of HHPs spanned from < 0.09 to 47.0 μg g^{-1}. Sample HD4 had an exceptionally high concentration compared with the other products investigated. On average, the level of Pb in household detergents surpassed that observed in other products. Soylak et al. [5] measured Pb concentrations of 9.2 to 21.6 μg g^{-1} in detergents from Turkey. Abulude et al. [19] reported Pb concentrations between 0.0 and −5.8 μg g^{-1} (mean 3.78 μg g^{-1}) in soaps and detergents from Nigeria. The concentration range for Pb observed in the samples analysed in this work was larger than that previously reported for Nigerian soaps and detergents. The levels of Pb in eight brands of the HHPs surpassed the Canadian limit (10.0 μg g^{-1}) for cosmetics [13], while only two brands of detergents exceeded the US FDA limit (20.0 μg g^{-1}) for Pb as an impurity in colour additives in cosmetics [21].

Chromium was detected at concentrations in the range of 0.4 to 43.7 μg g^{-1} in 11 out of 27 brands investigated. The remaining samples had Cr concentrations below the detection limit. Higher levels of Cr were found in HD8, HD9, HBS15 and HBS17 than the other HHPs. Chromium was found in higher concentrations in some of these samples than the 2.0 to 5.8 μg g^{-1} range reported for Cr in detergents in Turkey [5], 0.2 to 1.8 μg g^{-1} in Italy [22], and 0.5 to 2.7 μg g^{-1} found in soaps and detergents in Nigeria [19]. Studies have shown that Cr(III) and Cr (VI) can act as agents of contact allergies [23,24]. In Europe, 5.1% of reported cases of allergenic dermatitis have been associated with exposure to Cr. Cases of Cr contact allergy are more prevalent with age and occur more frequently in males than females [25,26]. Chromium (VI) permeates through skin more than Cr(III) due to the high solubility of Cr(VI) [27–29]. The permeation of chromium through the skin was found to depend on synthetic sweat at low pH, contact time and cleansers used [30]. Iyer et al. [23] found that a detergent bar with 40–50 μg g^{-1} of Cr(III) showed no form of allergic contact dermatitis in pre-sensitized subjects while Cr(VI) elicited contact dermatitis in these subjects.

The levels of Ni in these HHPs spanned from < 0.06 to 15.0 μg g^{-1}. The concentrations of Ni were higher in household detergents than household liquid soaps, bar soaps, hand sanitizers and hand creams. The highest sample concentration was found in HD10. Soylak et al. [5] reported Ni concentrations of 13.2 to 22.4 μg g^{-1} in detergents from Turkey which were somewhat higher than the levels found in our samples. Nickel concentrations of 1.2 to 2.0 μg g^{-1} have been reported for Ni in household detergents in Italy [22]. In 2007, Ni concentrations in detergents and soaps from Nigeria were reported as 1.30 to 3.10 μg

Table 3
Metal concentrations (μg g^{-1}) in household hygienic products.

	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Household detergents									
HD1	0.6 ± 0.3	4.5 ± 1.5	nd	3.5 ± 1.1	6.5 ± 0.1	7.0 ± 0.2	nd	24.5 ± 0.1	113 ± 0.1
HD2	0.8 ± 0.2	5.0 ± 3.0	nd	3.0 ± 0.2	7.0 ± 0.4	6.5 ± 0.3	3.0 ± 0.6	32.0 ± 1.4	124 ± 1.8
HD3	0.6 ± 0.2	3.5 ± 1.0	nd	4.0 ± 0.5	7.5 ± 0.1	7.5 ± 0.6	nd	51.5 ± 2.6	137 ± 0.7
HD4	5.4 ± 0.0	47.0 ± 2.0	nd	5.5 ± 0.1	8.0 ± 0.2	10.5 ± 0.3	7.0 ± 0.7	80.5 ± 3.7	322 ± 3.6
HD5	1.0 ± 0.0	5.5 ± 1.5	nd	4.0 ± 0.5	9.5 ± 0.1	12.5 ± 0.7	3.0 ± 1.0	53.5 ± 0.3	171 ± 1.9
HD6	1.5 ± 0.4	10.0 ± 1.0	nd	2.0 ± 0.1	6.5 ± 0.2	9.0 ± 1.4	nd	31.5 ± 0.3	129 ± 0.9
HD7	0.7 ± 0.3	9.0 ± 0.5	6.0 ± 28.6	4.0 ± 0.1	5.5 ± 0.1	8.0 ± 0.6	3.0 ± 0.5	23.0 ± 0.2	280 ± 3.3
HD8	0.9 ± 0.0	5.0 ± 1.5	32.2 ± 0.1	7.5 ± 0.5	7.5 ± 0.1	12.0 ± 1.2	14.5 ± 0.3	36.5 ± 1.5	201 ± 1.5
HD9	1.0 ± 0.2	16.5 ± 0.0	31.4 ± 0.25	2.5 ± 0.3	7.0 ± 0.7	12.0 ± 0.0	10.0 ± 1.4	51.5 ± 1.7	169 ± 0.5
HD10	1.8 ± 0.2	24.0 ± 3.0	1.0 ± 0.4	5.0 ± 0.3	9.5 ± 0.6	15.0 ± 1.2	12.0 ± 0.8	45.0 ± 0.6	189 ± 0.9
Household liquid soaps									
HLS11	2.5 ± 0.2	15.5 ± 1.5	2.9 ± 0.1	nd	1.0 ± 0.2	6.0 ± 1.8	nd	34.5 ± 1.3	62.4 ± 3.0
HLS12	1.7 ± 0.2	4.0 ± 0.0	3.5 ± 0.4	nd	1.0 ± 0.1	6.5 ± 0.2	0.5 ± 1.2	56.0 ± 4.1	92.9 ± 1.0
HLS13	0.4 ± 0.1	4.5 ± 1.0	1.3 ± 0.1	0.5 ± 0.2	5.0 ± 0.1	nd	5.0 ± 1.0	31.5 ± 4.8	79.7 ± 2.7
Household bar soaps									
HBS14	1.3 ± 0.0	2.5 ± 3.0	nd	2.0 ± 0.1	3.0 ± 0.1	6.0 ± 0.8	1.5 ± 1.6	48.5 ± 1.8	207 ± 2.7
HBS15	1.0 ± 0.0	7.0 ± 1.5	43.7 ± 0.7	3.5 ± 0.3	7.0 ± 0.0	11.5 ± 1.0	6.0 ± 1.1	40.5 ± 1.6	434 ± 5.3
HBS16	0.6 ± 0.2	5.5 ± 1.0	nd	1.5 ± 0.1	3.0 ± 0.1	6.0 ± 0.3	5.5 ± 0.2	38.5 ± 0.9	174 ± 0.0
HBS17	1.6 ± 0.1	2.0 ± 0.5	33.2 ± 0.8	2.5 ± 0.2	2.0 ± 0.2	7.0 ± 1.2	nd	31.0 ± 1.7	162 ± 0.4
HBS18	0.5 ± 0.1	0.5 ± 0.0	nd	2.0 ± 0.0	2.5 ± 0.5	7.0 ± 1.6	12.0 ± 0.6	42.5 ± 0.2	206 ± 2.5
HBS19	0.9 ± 0.1	2.5 ± 0.5	nd	3.5 ± 0.2	3.0 ± 0.1	6.0 ± 0.5	15.0 ± 1.4	675 ± 2.1	217 ± 0.0
HBS20	2.2 ± 0.1	2.5 ± 1.5	nd	nd	5.5 ± 0.3	7.5 ± 0.9	nd	31.5 ± 0.7	266 ± 1.8
HBS21	1.7 ± 0.1	15.5 ± 0.0	nd	11.5 ± 0.1	2.0 ± 0.6	5.0 ± 1.4	3.0 ± 1.7	9.0 ± 0.6	360 ± 4.2
Hand sanitizers									
HS22	1.6 ± 0.1	Nd	nd	nd	nd	6.5 ± 0.4	8.5 ± 2.1	40.5 ± 2.6	95.4 ± 3.4
HS23	1.6 ± 0.2	1.5 ± 0.8	nd	nd	nd	5.5 ± 0.2	5.0 ± 1.2	64.0 ± 0.7	145 ± 2.0
Spot-removing creams									
SRC24	1.4 ± 0.2	5.5 ± 0.5	nd	2.0 ± 0.4	1.5 ± 0.1	3.0 ± 0.1	nd	48.5 ± 8.2	221 ± 1.5
SRC25	1.2 ± 0.0	Nd	0.4 ± 0.3	1.0 ± 0.0	5.5 ± 0.1	2.0 ± 0.1	10.0 ± 0.6	400 ± 2.2	97.3 ± 4.5
Hand/body creams									
HBC26	1.7 ± 0.1	10.0 ± 1.0	0.4 ± 0.3	0.5 ± 0.1	6.0 ± 0.4	1.5 ± 0.7	24.5 ± 0.4	61.5 ± 0.4	144 ± 3.2
HBC27	1.6 ± 0.0	19.0 ± 0.0	nd	0.5 ± 0.2	2.5 ± 0.0	4.0 ± 0.2	nd	49.0 ± 7.7	207 ± 0.7

nd – not detected

g^{-1} [19]. Allergies associated with Ni are the most prevalent in patch-tests throughout Europe. The mean percentage of cases of contact allergies associated with Ni in 11 EU countries was 20.6% and Italy had the highest number (27.4%) of positive results [22]. Allergy to Ni is more prevalent in women than men possibly from the use of cosmetics, household cleansing products and jewellery [31–33]. Nickel allergy is associated with the capacity of Ni to bind with amino acid residues in proteins to produce Ni complexes [34]. The rate at which Ni diffuses through the stratum corneum is determined by the nature of the counter ions, oxidizing ability of sweat, exposure duration and dosage [28,35,36].

Cobalt concentrations in the HHPs varied from < 0.12 to 9.5 μg g^{-1}. In these samples, household detergents had higher levels of Co than the other types of products investigated. The levels of Co in these HHPs were lower than those found in Turkish detergents (9.8 to 17.8 μg g^{-1}) [5]. Mariani et al. [22] found Co levels below the LOQ in household detergents from Italy. In 2008, 7.9% of positive responses in cases of allergic contact dermatitis in 25,000 European subjects were due to exposure to Co [26]. Over the period 1970–1980, the contents of household consumer products were deemed to be the main cause of Co allergies in consumers [37]. The permeation of cobalt through the skin depends on the ability of sweat to oxidize metallic Co [28,30].

There are no international regulatory control limits for Cr, Ni, and Co in consumer products. However, Basketter et al. [38] have demonstrated that pre-sensitized subjects seldom react to Cr, Ni and Co concentrations below 10 μg g^{-1}. On the basis of these results, the authors suggested that the concentrations of these metals (Cr, Ni and Co) in consumer products should not exceed 5 μg g^{-1}, or for a better degree of protection, the levels of these metals should not exceed 1 μg g^{-1}. The concentrations of Cr in five brands, Co in 15 brands, and Ni in 22 brands, out of the 27 brands of HHPs examined, surpassed the technical avoidable limit of 5.0 μg g^{-1}. Ni and Co in the majority of the HHPs were present at concentrations that could illicit sensitization in pre-sensitized subjects.

Copper is an important element for metabolic activities in both humans and animals, but exposure to Cu through the use of copper intra-uterine devices has been responsible for increased menstrual blood loss and pain in women [39]. The concentrations of Cu in the household products investigated ranged from < 0.06 to 7.5 μg g^{-1}. The native black soap (HBS21) contained an exceptionally high concentration of Cu that was much greater than that in the other HHPs. On average, the Cu content of the detergents was higher than that of household bar soaps, liquid soaps and hand sanitizers. The copper concentrations in the HHPs are comparable with the levels found in Turkish detergents [5].

The levels of Zn in these HHPs ranged from 9.0 to 675 μg g^{-1}. The household bar soap HBS19 contained the highest concentration of Zn. Zinc concentrations in these samples were higher than those of Turkish detergents [3]. Although Zn is an essential nutrient to humans, its use in antidandruff shampoos has been implicated in allergic contact dermatitis [40]. Long-term exposure to high concentrations of Zn can lead to fragile hair and nails, and gastrointestinal and neurological disorders [10,41].

Manganese concentrations in these HHPs ranged from < 0.09 to 24.5 μg g^{-1}. On average, bar soaps had higher concentrations of Mn than detergents, liquid soaps and hand sanitizers. Soylak et al. [3] found Mn concentrations of 11.8 to 40.1 μg g^{-1} in detergents from Turkey which surpassed the levels found in these Nigerian consumer products. A risk of sensitization exists with the use of Cu and Mn in prosthetic materials in dentistry [42,43].

Iron is the most prominent element in these HHPs and its concentration varied from 62.4 to 434 μg g^{-1}. One brand of household bar

Table 4
Systemic exposure dosage (μg kg^{-1} bw day^{-1}) and margin of safety values for metals in household hygienic products determined by using a 50% bioaccessibility factor.

	Systemic Exposure Dosage (SED)								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Household detergents									
HD1	3.44×10^{-4}	2.58×10^{-3}	0.00	2.01×10^{-3}	3.73×10^{-3}	4.01×10^{-3}	0.00	1.40×10^{-2}	6.48×10^{-2}
HD2	4.59×10^{-4}	2.87×10^{-3}	0.00	1.72×10^{-3}	4.01×10^{-3}	3.73×10^{-3}	1.72×10^{-3}	1.83×10^{-2}	7.11×10^{-2}
HD3	3.44×10^{-4}	2.01×10^{-3}	0.00	2.29×10^{-3}	4.30×10^{-3}	4.30×10^{-3}	0.00	2.95×10^{-2}	7.85×10^{-2}
HD4	3.10×10^{-3}	2.69×10^{-2}	0.00	3.15×10^{-3}	4.59×10^{-3}	6.02×10^{-3}	4.01×10^{-3}	4.62×10^{-2}	1.85×10^{-1}
HD5	5.73×10^{-4}	3.15×10^{-3}	0.00	2.29×10^{-3}	5.45×10^{-3}	7.17×10^{-3}	1.72×10^{-3}	3.07×10^{-2}	9.80×10^{-2}
HD6	8.60×10^{-4}	5.73×10^{-3}	0.00	1.15×10^{-3}	3.73×10^{-3}	5.16×10^{-3}	0.00	1.81×10^{-2}	7.40×10^{-2}
HD7	4.01×10^{-4}	5.16×10^{-3}	3.44×10^{-3}	2.29×10^{-3}	3.15×10^{-3}	4.59×10^{-3}	1.72×10^{-3}	1.32×10^{-2}	1.61×10^{-1}
HD8	5.16×10^{-4}	2.87×10^{-3}	1.85×10^{-2}	4.30×10^{-3}	4.30×10^{-3}	6.88×10^{-3}	8.31×10^{-3}	2.09×10^{-2}	1.15×10^{-1}
HD9	5.73×10^{-4}	9.46×10^{-3}	1.80×10^{-2}	1.43×10^{-3}	4.01×10^{-3}	6.88×10^{-3}	5.73×10^{-3}	2.95×10^{-2}	9.69×10^{-2}
HD10	1.03×10^{-3}	1.38×10^{-2}	5.73×10^{-4}	2.87×10^{-3}	5.45×10^{-3}	8.60×10^{-3}	6.88×10^{-3}	2.58×10^{-2}	1.08×10^{-1}
Household liquid soaps									
HLS11	1.43×10^{-3}	8.89×10^{-3}	1.66×10^{-3}	0.00	5.73×10^{-4}	3.44×10^{-3}	0.00	1.98×10^{-2}	3.58×10^{-2}
HLS12	9.75×10^{-4}	2.29×10^{-3}	2.01×10^{-3}	0.00	5.73×10^{-4}	3.73×10^{-3}	2.87×10^{-4}	3.21×10^{-2}	5.33×10^{-2}
HLS13	2.29×10^{-4}	2.58×10^{-3}	7.45×10^{-4}	2.87×10^{-4}	2.87×10^{-3}	0.00	2.87×10^{-3}	1.81×10^{-2}	4.57×10^{-2}
Household bar soaps									
HBS14	7.45×10^{-4}	1.43×10^{-3}	0.00	1.15×10^{-3}	1.72×10^{-3}	3.44×10^{-3}	8.60×10^{-4}	2.78×10^{-2}	1.19×10^{-1}
HBS15	5.73×10^{-4}	4.01×10^{-3}	2.51×10^{-2}	2.01×10^{-3}	4.01×10^{-3}	6.59×10^{-3}	3.44×10^{-3}	2.32×10^{-2}	2.49×10^{-1}
HBS16	3.44×10^{-4}	3.15×10^{-3}	0.00	8.60×10^{-4}	1.72×10^{-3}	3.44×10^{-3}	3.15×10^{-3}	2.21×10^{-2}	9.98×10^{-2}
HBS17	9.17×10^{-4}	1.15×10^{-3}	1.90×10^{-2}	1.43×10^{-3}	1.15×10^{-3}	4.01×10^{-3}	0.00	1.78×10^{-2}	9.29×10^{-2}
HBS18	2.87×10^{-4}	2.87×10^{-4}	0.00	1.15×10^{-3}	1.43×10^{-3}	4.01×10^{-3}	6.88×10^{-3}	2.44×10^{-2}	1.18×10^{-1}
HBS19	5.16×10^{-4}	1.43×10^{-3}	0.00	2.01×10^{-3}	1.72×10^{-3}	3.44×10^{-3}	8.60×10^{-3}	3.87×10^{-1}	1.24×10^{-1}
HBS20	1.26×10^{-3}	1.43×10^{-3}	0.00	0.00	3.15×10^{-3}	4.30×10^{-3}	0.00	1.81×10^{-2}	1.53×10^{-1}
HBS21	9.75×10^{-4}	8.89×10^{-3}	0.00	6.59×10^{-3}	1.15×10^{-3}	2.87×10^{-3}	1.72×10^{-3}	5.16×10^{-3}	2.06×10^{-1}
Hand sanitizers									
HS22	4.59×10^{-3}	0.00	0.00	0.00	0.00	1.86×10^{-2}	2.44×10^{-2}	1.16×10^{-1}	2.73×10^{-1}
HS23	4.59×10^{-3}	4.30×10^{-3}	0.00	0.00	0.00	1.58×10^{-2}	1.43×10^{-2}	1.83×10^{-1}	4.16×10^{-1}
Spot-removing creams									
SRC24	2.17×10^{-2}	8.53×10^{-2}	0.00	3.10×10^{-2}	2.33×10^{-2}	4.66×10^{-2}	0.00	7.53×10^{-1}	3.43
SRC25	1.86×10^{-2}	0.00	6.21×10^{-3}	1.55×10^{-2}	8.53×10^{-2}	3.10×10^{-2}	1.55×10^{-1}	6.21	1.51
Hand/body creams									
HBC26	5.26×10^{-2}	3.10×10^{-1}	1.24×10^{-2}	1.55×10^{-2}	1.86×10^{-1}	4.64×10^{-2}	7.59×10^{-1}	1.90	4.46
HBC27	4.95×10^{-2}	5.88×10^{-1}	0.00	1.55×10^{-2}	7.74×10^{-2}	1.24×10^{-1}	0.00	1.52	6.41
Tolerable daily intake/ RDA	(0.35[a]) (1[b])	3.6	200*[b] (3.3)	5000*[c] (83)	100*[d] (1.7)	720**[d] (12)	10^{-18}**[e]	12000*[e]	12500*[e]

	Margin of Safety (MoS)								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Household detergents									
HD1	2.91×10^{5}	1.55×10^{5}	0.00	1.99×10^{6}	8.05×10^{3}	4.98×10^{5}	0.00	2.14×10^{6}	1.08×10^{6}
HD2	2.18×10^{5}	1.40×10^{5}	0.00	2.33×10^{6}	7.48×10^{3}	5.37×10^{5}	8.14×10^{6}	1.64×10^{6}	9.85×10^{5}
HD3	2.91×10^{5}	1.99×10^{5}	0.00	1.74×10^{6}	6.98×10^{3}	4.65×10^{5}	0.00	1.02×10^{6}	8.91×10^{5}
HD4	3.23×10^{4}	1.48×10^{4}	0.00	1.27×10^{6}	6.54×10^{3}	3.32×10^{5}	3.49×10^{6}	6.50×10^{5}	3.79×10^{5}

Table 4 (*continued*)

	Margin of Safety (MoS)								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
HD5	1.74×10^{5}	1.27×10^{5}	0.00	1.74×10^{6}	5.51×10^{3}	2.79×10^{5}	8.14×10^{6}	9.78×10^{5}	7.14×10^{5}
HD6	1.16×10^{5}	6.98×10^{4}	0.00	3.49×10^{6}	8.05×10^{3}	3.88×10^{5}	0.00	1.66×10^{6}	9.46×10^{5}
HD7	2.49×10^{5}	7.75×10^{4}	8.72×10^{4}	1.74×10^{6}	9.51×10^{3}	4.36×10^{5}	8.14×10^{6}	2.28×10^{6}	4.36×10^{5}
HD8	1.94×10^{5}	1.40×10^{5}	1.63×10^{4}	9.30×10^{5}	6.98×10^{3}	2.91×10^{5}	1.68×10^{6}	1.43×10^{6}	6.07×10^{5}
HD9	1.74×10^{5}	4.23×10^{4}	1.67×10^{4}	2.79×10^{6}	7.48×10^{3}	2.91×10^{5}	2.44×10^{6}	1.02×10^{6}	7.22×10^{5}
HD10	9.69×10^{4}	2.91×10^{4}	5.23×10^{5}	1.40×10^{6}	5.51×10^{3}	2.33×10^{5}	2.03×10^{6}	1.16×10^{6}	6.46×10^{5}
Household liquid soaps									
HLS11	6.98×10^{4}	4.50×10^{4}	1.80×10^{5}	0.00	5.23×10^{4}	5.81×10^{5}	0.00	1.52×10^{6}	1.96×10^{6}
HLS12	1.03×10^{5}	1.74×10^{5}	1.50×10^{5}	0.00	5.23×10^{4}	5.37×10^{5}	4.88×10^{7}	9.34×10^{5}	1.31×10^{6}
HLS13	4.36×10^{5}	1.55×10^{5}	4.03×10^{5}	1.40×10^{7}	1.05×10^{4}	0.00	4.88×10^{6}	1.66×10^{6}	1.53×10^{6}
Household bar soaps									
HBS14	1.34×10^{5}	2.79×10^{5}	0.00	3.49×10^{6}	1.74×10^{4}	5.81×10^{5}	1.63×10^{7}	1.08×10^{6}	5.90×10^{5}
HBS15	1.74×10^{5}	9.97×10^{4}	1.20×10^{4}	1.99×10^{6}	7.48×10^{3}	3.03×10^{5}	4.07×10^{6}	1.29×10^{6}	2.81×10^{5}
HBS16	2.91×10^{5}	1.27×10^{5}	0.00	4.65×10^{6}	1.74×10^{4}	5.81×10^{5}	4.44×10^{6}	1.36×10^{6}	7.02×10^{5}
HBS17	1.09×10^{5}	3.49×10^{5}	1.58×10^{4}	2.79×10^{6}	2.62×10^{4}	4.98×10^{5}	0.00	1.69×10^{6}	7.54×10^{5}
HBS18	3.49×10^{5}	1.40×10^{6}	0.00	3.49×10^{6}	2.09×10^{4}	4.98×10^{5}	2.03×10^{6}	1.23×10^{6}	5.93×10^{5}
HBS19	1.94×10^{5}	2.79×10^{5}	0.00	1.99×10^{6}	1.74×10^{4}	5.81×10^{5}	1.63×10^{6}	7.75×10^{4}	5.63×10^{5}
HBS20	7.93×10^{4}	2.79×10^{5}	0.00	0.00	9.51×10^{3}	4.65×10^{5}	0.00	1.66×10^{6}	4.59×10^{5}
HBS21	1.03×10^{5}	4.50×10^{4}	0.00	6.07×10^{5}	2.62×10^{4}	6.98×10^{5}	8.14×10^{6}	5.81×10^{6}	3.39×10^{5}
Hand sanitizers									
HS22	2.18×10^{4}	0.00	0.00	0.00	0.00	1.07×10^{5}	5.75×10^{5}	2.58×10^{5}	2.56×10^{5}
HS23	2.18×10^{4}	9.30×10^{4}	0.00	0.00	0.00	1.27×10^{5}	9.77×10^{5}	1.64×10^{5}	1.68×10^{5}
Spot-removing creams									
SRC24	4.60×10^{3}	4.69×10^{3}	0.00	1.29×10^{5}	1.29×10^{3}	4.30×10^{4}	0.00	3.99×10^{4}	2.04×10^{4}
SRC25	5.37×10^{3}	0.00	4.83×10^{4}	2.58×10^{5}	3.52×10^{2}	6.44×10^{4}	9.02×10^{4}	4.83×10^{3}	4.64×10^{4}
Hand/body creams									
HBC26	1.90×10^{3}	1.29×10^{3}	2.42×10^{4}	2.58×10^{5}	1.61×10^{2}	4.31×10^{4}	1.85×10^{4}	1.58×10^{4}	1.57×10^{4}
HBC27	2.02×10^{3}	6.80×10^{2}	0.00	2.58×10^{5}	3.88×10^{2}	1.61×10^{4}	0.00	1.98×10^{4}	1.09×10^{4}
Tolerable daily in-take/ RDA									

[a][46]; [b][47]; [c][48]; [d][11,49,50]; [e][51]; *μg per day; **mg per day; Values in parentheses refer to tolerable daily intake based on 60 kg adult.

Table 5
Systemic exposure dosage (μg kg^{-1} bw day^{-1}) and margin of safety values for metals in household hygienic products determined by using a 100% bioaccessibility factor.

	Systemic Exposure Dosage (SED)								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Household detergents									
HD1	6.88×10^{-4}	5.16×10^{-3}	0.00	4.01×10^{-3}	7.45×10^{-3}	8.03×10^{-3}	0.00	2.81×10^{-2}	1.30×10^{-1}
HD2	9.17×10^{-4}	5.73×10^{-3}	0.00	3.44×10-03	8.03×10^{-3}	7.45×10^{-3}	3.44×10^{-3}	3.67×10^{-2}	1.42×10^{-1}
HD3	6.88×10^{-4}	4.01×10^{-3}	0.00	4.59×10^{-3}	8.60×10^{-3}	8.60×10^{-3}	0.00	5.91×10^{-2}	1.57×10^{-1}
HD4	6.19×10^{-3}	5.39×10^{-2}	0.00	6.31×10^{-3}	9.17×10^{-3}	1.20×10^{-2}	8.03×10^{-3}	9.23×10^{-2}	3.69×10^{-1}
HD5	1.15×10^{-3}	6.31×10^{-3}	0.00	4.59×10^{-3}	1.09×10^{-2}	1.43×10^{-2}	3.44×10^{-3}	6.13×10^{-2}	1.96×10^{-1}
HD6	1.72×10^{-3}	1.15×10^{-2}	0.00	2.29×10^{-3}	7.45×10^{-3}	1.03×10^{-2}	0.00	3.61×10^{-2}	1.48×10^{-1}
HD7	8.03×10^{-4}	1.03×10^{-2}	6.88×10^{-3}	4.59×10^{-3}	6.31×10^{-3}	9.17×10^{-3}	3.44×10^{-3}	2.64×10^{-2}	3.21×10^{-1}
HD8	1.03×10^{-3}	5.73×10^{-3}	3.69×10^{-2}	8.60×10^{-3}	8.60×10^{-3}	1.38×10^{-2}	1.66×10^{-2}	4.19×10^{-2}	2.30×10^{-1}
HD9	1.15×10-03	1.89×10^{-2}	3.60×10^{-2}	2.87×10^{-3}	8.03×10^{-3}	1.38×10^{-2}	1.15×10^{-2}	5.91×10^{-2}	1.94×10^{-1}
HD10	2.06×10^{-3}	2.75×10^{-2}	1.15×10^{-3}	5.73×10^{-3}	1.09×10^{-2}	1.72×10^{-2}	1.38×10^{-2}	5.16×10^{-2}	2.17×10^{-1}
Household liquid soaps									
HLS11	2.87×10^{-3}	1.78×10^{-2}	3.33×10^{-3}	0.00	1.15×10^{-3}	6.88×10^{-3}	0.00	3.96×10^{-2}	7.16×10^{-2}
HLS12	1.95×10^{-3}	4.59×10^{-3}	4.01×10^{-3}	0.00	1.15×10^{-3}	7.45×10^{-3}	5.73×10^{-4}	6.42×10^{-2}	1.07×10^{-1}
HLS13	4.59×10^{-4}	5.16×10^{-3}	1.49×10^{-3}	5.73×10^{-4}	5.73×10^{-3}		5.73×10^{-3}	3.61×10^{-2}	9.14×10^{-2}
Household bar soaps									
HBS14	1.49×10^{-3}	2.87×10^{-3}	0.00	2.29×10^{-3}	3.44×10^{-3}	6.88×10^{-3}	1.72×10^{-3}	5.56×10^{-2}	2.37×10^{-1}
HBS15	1.15×10^{-3}	8.03×10^{-3}	5.01×10^{-2}	4.01×10^{-3}	8.03×10^{-3}	1.32×10^{-2}	6.88×10^{-3}	4.64×10^{-2}	4.98×10^{-1}
HBS16	6.88×10^{-4}	6.31×10^{-3}	0.00	1.72×10^{-3}	3.44×10^{-3}	6.88×10^{-3}	6.31×10^{-3}	4.41×10^{-2}	2.00×10^{-1}
HBS17	1.83×10^{-3}	2.29×10^{-3}	3.81×10^{-2}	2.87×10^{-3}	2.29×10^{-3}	8.03×10^{-3}	0.00	3.55×10^{-2}	1.86×10^{-1}
HBS18	5.73×10^{-4}	5.73×10^{-4}	0.00	2.29×10^{-3}	2.87×10^{-3}	8.03×10^{-3}	1.38×10^{-2}	4.87×10^{-2}	2.36×10^{-1}
HBS19	1.03×10^{-3}	2.87×10^{-3}	0.00	4.01×10^{-3}	3.44×10^{-3}	6.88×10^{-3}	1.72×10^{-2}	7.74×10^{-1}	2.49×10^{-1}
HBS20	2.52×10^{-3}	2.87×10^{-3}	0.00	0.00	6.31×10^{-3}	8.60×10^{-3}	0.00	3.61×10^{-2}	3.05×10^{-1}
HBS21	1.95×10^{-3}	1.78×10^{-2}	0.00	1.32×10^{-2}	2.29×10^{-3}	5.73×10^{-3}	3.44×10^{-3}	1.03×10^{-2}	4.13×10^{-1}
Hand sanitizers									
HS22	9.17×10^{-3}	0.00	0.00	0.00	0.00	3.73×10^{-2}	4.87×10^{-2}	2.32×10^{-1}	5.47×10^{-1}
HS23	9.17×10^{-3}	8.60×10^{-3}	0.00	0.00	0.00	3.15×10^{-2}	2.87×10^{-2}	3.67×10^{-1}	8.31×10^{-1}
Spot-removing creams									
SRC24	4.34×10^{-2}	1.71×10^{-1}	0.00	6.21×10^{-2}	4.66×10^{-2}	9.31×10^{-2}	0.00	1.51	6.86
SRC25	3.72×10^{-2}	0.00	1.24×10^{-2}	3.10×10^{-2}	1.71×10^{-1}	6.21×10^{-2}	3.10×10^{-1}	1.24×10^{1}	3.02
Hand/body creams									
HBC26	1.05×10^{-1}	6.19×10^{-1}	2.48×10^{-2}	3.10×10^{-2}	3.72×10^{-1}	9.29×10^{-2}	1.52	3.81	8.92
HBC27	9.91×10^{-2}	1.18	0.00	3.10×10^{-2}	1.55×10^{-1}	2.48×10^{-1}	0.00	3.03	1.28×10^{1}
Tolerable daily in-take/ RDA	(0.35[a]) (1[b])	3.6	200*[b] (3.3)	5000*[c] (83)	100*[d] (1.7)	720**[d] (12)	10^{-18}**[f]	12000*[f]	12500*[f]

	Margin of Safety (MoS)								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
Household detergents									
HD1	1.45×10^{5}	7.75×10^{4}	0.00	9.97×10^{5}	4.03×10^{3}	2.49×10^{5}	0.00	1.07×10^{6}	5.40×10^{5}
HD2	1.09×10^{5}	6.98×10^{4}	0.00	1.16×10^{6}	3.74×10^{3}	2.68×10^{5}	4.07×10^{6}	8.18×10^{5}	4.92×10^{5}
HD3	1.45×10^{5}	9.97×10^{4}	0.00	8.72×10^{5}	3.49×10^{3}	2.33×10^{5}	0.00	5.08×10^{5}	4.46×10^{5}

Table 5 (*continued*)

	Margin of Safety (MoS)								
	Cd	Pb	Cr	Cu	Co	Ni	Mn	Zn	Fe
HD4	1.61×10^{4}	7.42×10^{3}	0.00	6.34×10^{5}	3.27×10^{3}	1.66×10^{5}	1.74×10^{6}	3.25×10^{5}	1.90×10^{5}
HD5	8.72×10^{4}	6.34×10^{4}	0.00	8.72×10^{5}	2.75×10^{3}	1.40×10^{5}	4.07×10^{6}	4.89×10^{5}	3.57×10^{5}
HD6	5.81×10^{4}	3.49×10^{4}	0.00	1.74×10^{6}	4.03×10^{3}	1.94×10^{5}	0.00	8.31×10^{5}	4.73×10^{5}
HD7	1.25×10^{5}	3.88×10^{4}	4.36×10^{4}	8.72×10^{5}	4.76×10^{3}	2.18×10^{5}	4.07×10^{6}	1.14×10^{6}	2.18×10^{5}
HD8	9.69×10^{4}	6.98×10^{4}	8.13×10^{3}	4.65×10^{5}	3.49×10^{3}	1.45×10^{5}	8.42×10^{5}	7.17×10^{5}	3.04×10^{5}
HD9	8.72×10^{4}	2.11×10^{4}	8.33×10^{3}	1.40×10^{6}	3.74×10^{3}	1.45×10^{5}	1.22×10^{6}	5.08×10^{5}	3.61×10^{5}
HD10	4.84×10^{4}	1.45×10^{4}	2.62×10^{5}	6.98×10^{5}	2.75×10^{3}	1.16×10^{5}	1.02×10^{6}	5.81×10^{5}	3.23×10^{5}
Household liquid soaps									
HLS11	3.49×10^{4}	2.25×10^{4}	9.02×10^{4}	0.00	2.62×10^{4}	2.91×10^{5}	0.00	7.58×10^{5}	9.78×10^{5}
HLS12	5.13×10^{4}	8.72×10^{4}	7.48×10^{4}	0.00	2.62×10^{4}	2.68×10^{5}	2.44×10^{7}	4.67×10^{5}	6.57×10^{5}
HLS13	2.18×10^{5}	7.75×10^{4}	2.01×10^{5}	6.98×10^{6}	5.23×10^{3}	0.00	2.44×10^{6}	8.31×10^{5}	7.66×10^{5}
Household bar soaps									
HBS14	6.71×10^{4}	1.40×10^{5}	0.00	1.74×10^{6}	8.72×10^{3}	2.91×10^{5}	8.14×10^{6}	5.39×10^{5}	2.95×10^{5}
HBS15	8.72×10^{4}	4.98×10^{4}	5.99×10^{3}	9.97×10^{5}	3.74×10^{3}	1.52×10^{5}	2.03×10^{6}	6.46×10^{5}	1.41×10^{5}
HBS16	1.45×10^{5}	6.34×10^{4}	0.00	2.33×10^{6}	8.72×10^{3}	2.91×10^{5}	2.22×10^{6}	6.80×10^{5}	3.51×10^{5}
HBS17	5.45×10^{4}	1.74×10^{5}	7.88×10^{3}	1.40×10^{6}	1.31×10^{4}	2.49×10^{5}	0.00	8.44×10^{5}	3.77×10^{5}
HBS18	1.74×10^{5}	6.98×10^{5}	0.00	1.74×10^{6}	1.05×10^{4}	2.49×10^{5}	1.02×10^{6}	6.16×10^{5}	2.96×10^{5}
HBS19	9.69×10^{4}	1.40×10^{5}	0.00	9.97×10^{5}	8.72×10^{3}	2.91×10^{5}	8.14×10^{5}	3.88×10^{4}	2.81×10^{5}
HBS20	3.96×10^{4}	1.40×10^{5}	0.00	0.00	4.76×10^{3}	2.33×10^{5}	0.00	8.31×10^{5}	2.29×10^{5}
HBS21	5.13×10^{4}	2.25×10^{4}	0.00	3.03×10^{5}	1.31×10^{4}	3.49×10^{5}	4.07×10^{6}	2.91×10^{6}	1.70×10^{5}
Hand sanitizers									
HS22	1.09×10^{4}	0.00	0.00	0.00	0.00	5.37×10^{4}	2.87×10^{5}	1.29×10^{5}	1.28×10^{5}
HS23	1.09×10^{4}	4.65×10^{4}	0.00	0.00	0.00	6.34×10^{4}	4.88×10^{5}	8.18×10^{4}	8.42×10^{4}
Spot-removing creams									
SRC24	2.30×10^{3}	2.34×10^{3}	0.00	6.44×10^{4}	6.44×10^{2}	2.15×10^{4}	0.00	1.99×10^{4}	1.02×10^{4}
SRC25	2.69×10^{3}	0.00	2.42×10^{4}	1.29×10^{5}	1.76×10^{2}	3.22×10^{4}	4.51×10^{4}	2.42×10^{3}	2.32×10^{4}
Hand/body creams									
HBC26	9.50×10^{2}	6.46×10^{2}	1.21×10^{4}	1.29×10^{5}	8.07×10^{1}	2.15×10^{4}	9.23×10^{3}	7.88×10^{3}	7.85×10^{3}
HBC27	1.01×10^{3}	3.40×10^{2}	0.00	1.29×10^{5}	1.94×10^{2}	8.07×10^{3}	0.00	9.89×10^{3}	5.46×10^{3}
Tolerable daily in-take/ RDA									

[a][42]; [b][43]; [c][43]; [d][7,45,46]; [e][47]; *μg per day; **mg per day; Values in parentheses refer to tolerable daily intake based on 60 kg adult.

soap (HBS15) contained the highest level of Fe. Generally, the detergent and bar soap samples had higher concentrations of Fe than the liquid soap samples. The Fe concentrations in our samples surpassed those found in Turkish detergents (19.1–60.1 μg g^{-1}) [17]. Iron is an essential nutrient in humans and animals, and its deficiency in the human body can induce anaemic conditions, but studies have shown that cellular death can arise from human exposure to Fe in cosmetics [44] or colorectal cancer [45] as a result of cumulative effects.

3.1. Safety evaluation

The calculated SED values to metals arising from the use of these HHPs in comparison with their respective provisional tolerable daily intake (PTDI) values, or recommended dietary allowance (RDA) values in the case of Mn, Zn and Fe, are listed in Tables 4 and 5. The SED values for Cd, Pb, Cr, Cu, Ni and Co were below their PTDI values even at 100% systemic availability. In addition, the estimated SEDs for Fe, Mn, and Zn were also less than their respective recommended dietary allowance values even at 100% systemic availability. In this study, we adopted a PTDI of 3.6 μg Pb kg^{-1} bw day^{-1} as the indicative value for comparison with our results despite its withdrawal in 2011 by the FAO/WHO as "it could no longer be considered health protective" [52]. In the present study, the spot removers and hand creams had higher SED values for the metals investigated than did hand sanitizers, soaps and detergents. The SED values for the metals were in the order: Fe > Zn > Pb > Ni > Co > Cu > Cd > Mn > Cr. The highest SED values of Cd and Pb at 100% systemic availability accounted for 31% and 32% of the EFSA PTDI value of 0.35 μg Cd kg^{-1} bw day^{-1} [42] and the indicative value of 3.6 μg Pb kg^{-1} bw day^{-1} respectively. These values are somewhat high for a single exposure source, although 100% systemic availability is a worst-case setting and nearly impossible in real-life exposure scenarios. For the other metals, the SED values were below 24% of their respective PTDI/RDA values even at 100% systemic availability. The MoS values for the investigated metals were greater than 100 (Tables 4 and 5) which suggests that these HHPs are reasonably safe to use without adverse effects despite the prevalence of significant levels of toxic (Cd and Pb), allergenic (Ni, Cr and Co) and other low toxicity metals (Mn, Zn and Fe).

4. Conclusions

The HHPs investigated can be considered safe for use by humans without causing deleterious effects. However, these products contain significant levels of toxic (Cd and Pb), allergenic (Ni, Cr and Co) and other low toxicity metals (Mn, Zn and Fe) which could be a potential threat to the environment since the effluents from washing processes are sometimes discharged directly into the environment with little or no treatment. Therefore, there is a need for caution in the use of these products, and for a careful selection of raw materials, branding and production processes. This is to be done with the aim of reducing the levels of the metallic content in these products to near zero, and also the consequent human exposure to these contaminants from the use of these products, as well as to minimize the effect of bathing and laundry effluents on the ecosystem.

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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