Study of Controlled Migration of Cadmium and Lead Into Foods From Plastic Utensils for Children

Elizeu Chiodi Pereira
Universidade de Sao Paulo Faculdade de Saude Publica https://orcid.org/0000-0003-3808-760X
Isabelle Nogueira Leroux
University of Sao Paulo Campus of Sao Paulo: Universidade de Sao Paulo
Maciel Santos Luz
Institute for Technological Research: Instituto de Pesquisas Tecnologicas
Bruno Batista Lemos
Federal University of the ABC: Universidade Federal do ABC
Kelly Polido Kaneshiro Olympio (kellypko@usp.br)
University of Sao Paulo: Universidade de Sao Paulo

Research Article

Keywords: Lead, Cadmium, plastic utensils, specific migration, children, potentially toxic metals

Posted Date: November 8th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-973552/v1

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on March 11th, 2022. See the published version at https://doi.org/10.1007/s11356-022-19433-2.

Abstract

Lead is a highly neurotoxic chemical element known for reducing intelligence quotient (IQ) and promoting antisocial behavior in children and adolescents, while cadmium is a carcinogenic bioaccumulative element. Contaminated foods and beverages are the most common routes of exposure. The objective of this study was to determine Cd and Pb concentrations in colored plastic utensils for use by children and to measure the specific migration of these elements into beverages and foods. Pb and Cd concentrations were determined using a handheld XRF. Specific migration tests were conducted using the simulant solutions. Migration levels were determined by ICP-MS and migration tests for Pb were also performed on actual samples GF-AAS determination. Utensils (n=87) were purchased for containing Cd and/or Pb concentrations above permitted limits. The mean of Pb and Cd were 1110 and 338 ppm respectively. For specific migration assays, Pb levels were 187, 13 and 380 times above the permitted limit for acetic acid, water and orange juice, respectively. Cd levels 50 and 2.4 times above the permitted limit for acetic acid and water, respectively. The districts where the utensils were purchased were grouped according to their Social Vulnerability Index and compared using ANOVA. Results revealed a group difference in mean Pb levels for low versus medium/high social vulnerability ($p = 0.006$). The findings corroborate the initial hypothesis that these utensils constitute a major source of exposure to PTEs such as Cd and Pb.

1. Introduction

Testing for the presence of Potentially Toxic Elements (PTEs), such as lead, in ceramic domestic utensils dates back to the 1960s (Huzl et al. 1960). Demont et al (2012) found that the solubility of metals, and their respective formation of complexes, plays a key role in the lixiviation of metal ions from the surface of materials, whereby changes in pH and temperature influence the specific migration of these ions into foods and beverages upon surface contact with utensils.

Contamination from plastic toys is one of the most important potential routes of exposure to toxic metals such as cadmium (Cd) and lead (Pb). Greenway and Gerstenberger (2010), in an evaluation of plastic toys from day care centers in Las Vegas (USA), found that 5.4% of the toys tested had Pb concentrations above levels permitted by local legislation, particularly yellow items. In Colombia, researchers detected levels of Pb in brown, orange and yellow paints from plastic toys that exceeded permitted limits (Mateus-García and Ramos-Bonilla, 2014).

In Brazil, environmental exposure of children aged 1-4 years was evaluated both in households and day care centers in São Paulo. Results of the study found that over 50 toys contained Pb concentrations exceeding those allowed by Brazilian law, which stipulates a limit of 600 ppm for lead (Silva et al 2018; Brazil 2008). Similarly, the presence of these and other toxic metals in plastic toys has been reported in many countries, including Kazakhstan (Akimzhanova et al. 2020), China (Kang and Zhu 2015; Cui et al. 2015) and the UK (Turner 2018).

Regarding Pb, the toxic effects of this metal in the organism of children have been associated with learning difficulties, attention deficit, low intelligence quotient (IQ) and anti-social behavior (Bellinger, 2004; Needleman, 2004; Lanphear et al 2005; Hornung et al. 2009; Mazumdar et al. 2011; Dickerson et al. 2016; Blackwoicz et al. 2016; Wagner et al. 2016, Olympio et al. 2009; Olympio et al. 2010; Olympio et al. 2017). Lead contamination can occur during the food production process through to specific migration from packaging into the foods contained (Kiyataka et al. 2014). With regard to Cd, the main toxicological effects include renal damage, hypertension, emphysema, malformation, and impaired reproductive function (Magna et al. 2014). Exposure to Cd can take place through occupational activities involving contact with the metal (OSHA 2013, Salles et al. 2021) and by ingesting foods contaminated by this element (Rahimzadeh et al. 2017).

Thus, child exposure to these metals is a global health problem, where children are especially vulnerable both because of their hand-to-mouth behavior and the fact their gastrointestinal and nervous systems are undergoing development (Olympio et al. 2009; Li et al. 2016; Tamayo et al. 2016). Ingestion is therefore the main route of exposure to Cd and Pb where, in the case of Pb, food ingestion accounts for 80% of exposure to the element (Li et al. 2016). Moreover, Cd and Pb both feature in the list of 10 chemicals of public health concern (WHO 2010), due to their toxic effects on the body, even at low levels.

Thus, the objective of this study was to determine Cd and Pb concentrations in colored plastic utensils for use by children during feeding and to measure the levels which migrate from the utensils into foods and beverages.

2. Materials And Methods

2.1. Description of materials

The objects of study were colored plastic utensils including cups, mugs, bowls and feeding bottles intended for use by children. The materials were purchased between March and June 2018 at major commercial centers located in the districts of Lapa, Pinheiros, Capão Redondo, São Miguel and Pari in the cities of São Paulo and Osasco, Greater São Paulo, Brazil. All of the utensils purchased were low-cost (≤ $1 USD).

2.2. Analysis using X-Ray fluorescence spectrometry (XRF)

Concentrations of Cd and Pb in the utensils were quantified *in loco* using a hand-held analyzer of metal alloys with coupled XRF (model Niton XL2 Analyzer, Thermo Scientific). The device was calibrated after each start-up employing a certified calibration standard based on the EN-71-3:2013, in accordance with the manufacturer´s specifications. The arithmetic mean was calculated using $LOD/\sqrt{2}$ for values below the LOD (10 ppm for Pb and 20 ppm for Cd).

All utensils exhibiting concentrations exceeding 90 ppm and 75 ppm (US 1995; WHO 2010) for lead and cadmium, respectively, were purchased. The limit established in Brazilian law is 600 ppm for Pb (Brazil

2008). Since no values have been defined in Brazil for Cd limits, U.S. legislation was adopted to define these parameters for the purposes comparing the study results.

Materials containing Cd and Pb at concentrations above the limits allowed under U.S. law were sent to the laboratory. The materials were first washed with Extran detergent to remove any soot layer and then rinsed in deionized water. After the cleaning procedure, the items were analyzed by XRF in triplicate, with measurements taken at different points of the utensil to improve determinations of contamination by these elements.

2.3. Specific migration tests for Cd and Pb

The specific migration assays were carried out on a sub-sample of 11 cups and mugs containing the highest concentrations of Cd and Pb, observing EN 1186-1:2002 and EN 1186-3:2002 recommended by Resolution 52/10 of the Brazilian Health Surveillance Agency - ANVISA (Brazil 2010).

Using a diamond tipped band saw, 1 cm^2 fragments of each of the 11 utensils were removed and subsequent rewashed. Simulant solutions used were 15 mL of water and 15 mL of acetic acid 3% (m/v). The fragments were submerged separately in these solutions for 10 days at ambient temperature (25ºC controlled in clean room – ISO Class 8) using 50 mL conical polypropylene tubes. Analytical blanks were prepared simulating the same conditions as the migration assays and all sample preparations were also carried out in the clean room.

After the contact period had elapsed, Cd and Pb concentrations in the simulant solutions were determined in triplicate by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Agilent 7900, Hachioji, Japan). Total concentrations of these elements in the plastic utensils were calculated based on the ratio of total surface area of the cups and mugs to their respective fragments.

2.4. Specific migration tests for commercial beverages

Additionally, specific migration assays for Pb were performed using commercially available beverages from supermarket outlets for 4 of the utensils exhibiting the highest lead concentrations. Solutions for specific migration were cola soft-drink (Coca-Cola™), vinegar (Castelo), processed orange juice (Xandô) and milk (Italac). The tests were conducted according to the procedures outlined earlier. Concentrations of Pb in the solutions were analyzed by GF graphite-furnace atomic absorption spectrometry (GF-AAS) (Model Varian GTA120 AA 240FS).

2.5. Statistical analyses

For statistical treatment, the Paulista Social Vulnerability Index (IPVS) for each district where utensils were purchased was referenced. According to the Foundation State System of Data Analysis (SEADE 2010), the IPVS conveys information on the highest and lowest social vulnerability conditions to which a population is exposed. The index comprises 5 classes of vulnerability, as depicted in Figure 1.

As shown in Figure 1, the IPVS was 1 (extremely low social vulnerability) for the districts of Pinheiros and Lapa, 2 (low social vulnerability) for the district of Pari and city of Osasco, 4 (medium social vulnerability) for the district of São Miguel and 5 (high social vulnerability) for the district of Capão Redondo. These results were pooled into 3 groups: Group 1 (IPVS = 1), Group 2 (IPVS = 2) and Group 3 (IPVS = 4 + IPVS = 5). For Group 3, the districts of São Miguel and Capão Redondo were pooled together because their socioeconomic characteristics were similar.

The analysis of variance (ANOVA) test (95% confidence interval) was performed to compare mean Pb and Cd values measured for each region and group. The Stata 14 software package was employed for all statistical analyses.

3. Results

3.1. Analyses by XRF

A total of 674 plastic utensils were analyzed using XRF as per the procedures described in Methods. The Cd and Pb concentrations in most of the utensils tested proved below the limit of detection. The distribution of utensils and percentage with detectable concentrations by type are presented in Table 1 below.

Table 1
Distribution and percentage of plastic utensils by type

	Total samples analyzed N (%)	**Samples with detectable concentrations N (%)**	**Pb N (%)**	**Cd N (%)**
Cups	270 (40.06)	122 (42.51)	120 (43.01)	27 (47.37)
Mugs	174 (25.81)	65(22.65)	61(21.86)	10 (17.54)
Plates	107 (15.87)	52 (18.12)	51(18.28)	15 (26.32)
Bowls	103(15.28)	38 (13.24)	37 (13.26)	5 (8.80)
Feeding bottles	20 (2.970)	10 (3.48)	10 (3.58)	-
Total	**674 (100)**	**287 (100)**	**279 (100)**	**57 (100)**

Of the total 674 utensils analyzed, 87 were purchased for exhibiting Pb and/or Cd concentrations above the limit permitted by U.S. law (90 ppm and75 ppm, respectively). The means, standard deviations and minimum and maximum values for Pb concentrations in the plastic utensils, by type and color, are shown in Table 2.

Table 2
Mean, standard deviation, and minimum and maximum Pb concentrations, in ppm, by utensil type and color

	N	%	Mean	SD*	Minimum	Maximum
Utensil color						
Red	30	34	942	1288	185	5989
Yellow	9	10	1930	2685	91	8166
Orange	8	9	2296	2050	260	5601
Green	32	37	943	1526	104	7017
Black	5	6	291	280.5	125	783
Other colors	3	3	323	177	167	515
Total	**87**	**100**	**1110**	**1642**	**91**	**8166**
Utensil type						
Cups	33	38	1235	1751	91	7107
Mugs	19	22	758	992	130	4027
Plates	18	21	776	1856	107	8166
Bowls	11	13	2048	1943	173	5989
Feeding bottles	6	7	821	981	171	2579
Total	**87**	**100**	**1110**	**1642**	**91**	**8166**

* Standard deviation

The mean Pb concentration for the utensils purchased (n=87) was 1110 ppm. Based on the 600 ppm limit for Pb established under Brazilian law (Brazil 2008), 34 utensils exceeded the limit, exhibiting a mean Pb concentration of 2443 ppm.

Of the 87 plastic utensils purchased, 15 contained Cd concentrations exceeding the limit allowed by U.S. law. The means, standard deviations and minimum and maximum values for Cd concentrations in the plastic utensils, by type and color, are shown in Table 3.

Table 3
Mean, standard deviation, and minimum and maximum Cd concentrations, in ppm, by utensil type and color

	N	%	Mean	SD*	Minimum	Maximum
Utensil color						
Red	8	53	224	120	81	352
Yellow	2	13	198	70	148	247
Green	4	27	596	552	83	1195
Pink	1	7	195	-	-	-
Total	**15**	**100**	**318**	**321**	**81**	**1195**
Utensil type						
Cups	7	47	336	384	83	1995
Mugs	5	33	260	119	81	352
Plates	3	20	370	488	88	993
Total	**15**	**100**	**318**	**321**	**81**	**1195**
* Standard deviation						

Mean concentrations and number of utensils containing Pb and Cd concentrations above legal limits for commercial centers visited in Greater São Paulo are given in Table 4.

Table 4
Distribution of mean Cd and Pb concentrations, in ppm, and number of utensils, according to their concentrations, by geographic area in which they were purchased

	No. of items analyzed	***Mean Pb ± SD***	***% items with Pb > 90 ppm***	***% items with Pb > 600 ppm***	***Mean Cd ± SD***	***% items with Cd > 75 ppm***
Lapa	82	161.97 ± *685.41*	7.3	4.9	18.50±*39.14*	1.2
Pinheiros	69	142.55 ± *768.62*	7.2	5.8	18.50±*39.14*	1.4
Osasco	165	298.78±*1021.20*	17.6	9.7	20.87±*34.76*	3.6
Capão Redondo	106	35.73±*119.17*	7.5	0.9	23.50±*88.88*	0.9
São Miguel	138	*72.80±209.27*	15.2	4.3	37.66±*143.90*	5.1
Pari	114	135.60±*461.83*	22.8	4.4	20.53±*24.50*	1.8

Of the regions visited, the district of Pari had the highest percentage (22.8%) of utensils exhibiting Pb concentrations above recommended levels by U.S. law. By contrast, in the district of Pinheiros, only 7.2% of utensils contained concentrations exceeding this limit. The highest percentage of utensils exceeding legal limits for Pb were those purchased in the city of Osasco, the region with the highest mean Pb level. Mean Cd concentrations were very similar across districts, and remained within legal limits. For Pb, however, only the districts of Capão Redondo and São Miguel had mean concentrations below 90 ppm for the element.

Group 1 (IPVS =1, Pinheiros and Lapa) had mean Pb of 153.09 ± 722.21 and mean Cd of 18.57 ± 38.35; Group 2 (IPVS = 2, Osasco and Pari) mean Pb of 232.10 ±176.54 and mean Cd of 20.73 ± 30.93; and Group 3 (IPVS = 4 + IPVS = 5, São Miguel and Capão Redondo) had a mean Pb of 56.65 ±176.54 and mean Cd of 31.51 ± 123.03 ppm.

Comparison of the groups showed no statistically significant difference for Cd, whereas a significant difference was found among the groups for Pb (p=0.0089), particularly Groups 2 and 3 (p=0.06) on ANOVA. There was a major disparity between these groups for income, where the value for Group 2 was 3 times higher than for Group 3.

3.2. Specific migration tests for simulant solutions

The types of plastic utensils (n=11) used in the migration assays, along with overall mean and standard deviation for concentrations of the metals (ppm), are given in Table 5. The concentrations shown were derived from the XFR analyses of these utensils.

Table 5
Types of plastic utensils by color and mean Pb and Cd concentrations (ppm) for 11 utensils used in specific migrations assays

Utensil type	Color	Pb concentration	Cd concentration
Mugs (n=6)	Orange	4535	<LOD
	Pink	<LOD	195
	Green	4027	<LOD
	Red	188	352
	Red	2579	<LOD
	Red	965	<LOD
Cups (n=5)	Orange	4662	<LOD
	Orange	5901	<LOD
	Green	7107	<LOD
	Red	559	263
	Red	440	244
Mean and SD*		2815.33 ± 2545.30	101.35 ± 133.50
* Standard deviation			

The mean Pb values as measured by XRF analyses shown in Table 5 are almost 32 times over the limit allowed by U.S. law, whereas Cd is 1.4 times greater.

For specific migration of these metals, Brazilian law stipulates limits of 0.005 $mg.kg^{-1}$ and 0.01 $mg.kg^{-1}$ for Cd and Pb, respectively (Brazil 2010b).

For Pb, concentrations migrating to simulant solutions were 187 times greater than the legal limit for acetic acid and 13 times greater for water. Concentrations of Cd exceeded permitted limits by 50.2 and 2.4 times for acetic acid and water, respectively. The results for the specific migration tests are shown in Table 6.

Table 6

Cd and Pb concentrations (mg.kg^{-1}) for specific migration tests in plastic utensils exhibiting highest levels *in loco* (n=11)

	Acetic acid	**Water**
Pb		
Mean	1.87	0.13
Minimum	<LOD	<LOD
Maximum	5.46	0.44
Migration limit	0.01	0.01
% samples > migration limit	90.90	90.9
Cd		
Mean	0.251	0.012
Minimum	0.004	<LOD
Maximum	1.505	0.041
Migration limit	0.005	0.005
% samples > migration limit	90.91	54.55

* LOD < 0.001 ug.kg^{-1}.

Even when water was employed as the simulant solution, over 90% of samples exhibited specific migration values that exceeded the legal limit for Pb. For cadmium, migration values exceeded the limit in 54.55% of samples.

3.3. Specific migration tests for Pb – commercial beverages

Results of specific migration tests for lead in cola, vinegar, orange juice and milk are given in Table 7 below.

Table 7

Pb migration concentrations (mg.kg-1) into simulants cola, vinegar, orange juice and milk

Sample	Migration concentration into simulant for sample area	Standard Deviation	Migration concentration into simulant for total area of utensil
Coca-Cola	0.0131	0.0003	1.43
Vinegar	0.0144	0.0003	1.57
Orange juice	0.0348	0.0020	3.80
Milk	0.0058	0.0002	0.63

Based on the area of samples (1 cm^2), for orange juice Pb migration proved 28.74% higher than the legal limit. For the total surface area of the utensil, this value represents a migration level 380 times greater than permitted limits. The specific migration levels of Pb were above permitted limits for all the beverages tested.

4. Discussion

To the best of our knowledge, this is the first study investigating colored plastic food utensils as a potential source of Cd and Pb exposure in children, with no other studies of these plastic materials available in the literature. In the present study, the results showed that high concentrations of these metals determined by XRF had major potential for specific migration into simulant solutions and commercial beverages. Similar studies have been conducted involving plastic packaging for storing foods. Kiyataka et al. (2014) detected Pb levels of 30-40 $mg.kg^{-1}$ using specific migrations tests, whereas cadmium concentrations proved below the limit of detection for the method.

Of the 674 items analyzed in the present study, 287 contained detectable concentrations of the metals (Table 1) and, of this total, 87 had levels which exceeded permitted limits. It is important to emphasize, however, that while levels in some items tested were within allowed limits, this does not rule out the possibility of samples containing some degree of contamination by Cd, Pb or other PTE not measured in this study.

The XRF results (Tables 1-4) were cause for concern, revealing mean Cd and Pb concentrations far exceeding limits allowed by U.S. and Brazilian law (Brazil 2008; US 1997; WHO 2010). A number of studies have been carried out on plastic toys as a source of exposure. Greenway and Gerstenberger (2010) evaluated lead contamination using XRF in toys from 50 day care centers in the USA. Results showed around 5.4% contained concentrations that exceeded legally allowed limits, with yellow items exhibiting the highest lead levels. The present study found the highest Cd concentration in green items (Table 3) and the highest Pb levels in orange and yellow utensils (Table 2). According to the National

Institution of Metrology, Quality and Technology (INMETRO 2015), inorganic lead-based pigment can be used to confer paints yellow, orange and red hues. These pigments represent a low-cost option compared to other types of pigmentation, perhaps explaining the high concentrations of these metals in colored utensils.

Although the highest percentage of utensils exceeding the legal limit for lead (22.8%) were found in the district of Pari, the highest mean Pb concentrations were found in the city of Osasco, where both these regions had similar socioeconomic characteristics according to their IPVS. The ANOVA results showed a statistically significant difference between Groups 2 and 3 ($p = 0.006$). This finding was expected, given that mean Pb values for the Group 2 regions of Osasco and Pari were 4 times higher than those detected in the Group 3 districts of São Miguel and Capão Redondo (Group 3), despite the higher IPVS of the latter. Other factors to take into account include the low cost of the utensils and the location in which they were purchased, constituting major commercial hubs of Greater São Paulo. Socioeconomic aspects such as educational level, income bracket, besides other factors, are known to be directly associated with a host of chemical exposure scenarios (Carvalho et al. 2017). Shoppers often travel to these commercial centers to buy this type of product and thus exposure to these Pb and Cd-contaminated items extends beyond the local population.

The highest migrations were detected for acetic acid 3% solution (m/v), with 99.9% of utensils exhibiting specific migration that exceeded permitted limits for both Cd and Pb (Table 6). Whitt et al. (2015) investigated specific migration of heavy metals from recycled polyethylene terephthalate using deionized water as the simulant solution. The levels of Cd and Pb which migrated into the simulant proved below the limit of detection of the method. In the present study, levels of migration of Cd exceeded allowed limits for 54.55% of the utensils tested, with an even higher proportion for Pb, at around 91% of items tested. All of the migration test results using simulant solutions exceeded the allowed levels established by Brazilian law of 0.005 $mg.kg^{-1}$ and 0.01 $mg.kg^{-1}$ for Cd and Pb, respectively. No contamination was detected in the analytical blanks, thus confirming the major potential bioaccessibility of the metals previously quantified *in loco* using XRF analyses (Table 5).

The migration tests on consumable beverages were performed for Pb only. The results found for these tests were even more alarming (Table 7). For orange juice, migration values were 360 times higher than the legally allowed limit, while all the other beverages also exceeded migration limits on tests for sample fragment area and overall area of both cups and mugs. These beverages were chosen because they are routinely consumed by children using the utensils in both home and school environments, where children can spend up to 10 hours a day at day care centers (Olympio et al. 2018). Notably, the analyses of commercial beverages showed they contained Pb and Cd levels which were below the limit of detection.

Many authors have implicated plastic objects as potential sources of exposure. Turner (2018) analyzed around 200 toys made of recycled plastics in the European Union and found high levels of PTEs in the base material. In a study conducted in Kazakhstan, Akimzhanova et al. (2020) found levels of lead contamination in children´s plastic jewelry of 50 $mg.kg^{-1}$. Guney and Zagury (2013) investigated bioaccessibility of both Pb and Cd in plastic toys and found values in the 642-647 mg.kg^{-1} range for Pb and 1.31-1.34 mg.kg^{-1} for Cd. In a Chinese study of specific migration of lead in plastic toys, Kang and Zhu (2015) found a level of 95 mg.kg^{-1}. Cui et al. (2015), in a study of bioaccessibility of Pb in toys from the Chinese market, found levels of 3.19 mg.kg^{-1} for Pb and 0.86 mg.kg^{-1} for Cd. All of the above-cited studies, consistent with the present investigation, confirmed plastic toys and jewelry as a potential source of Cd and Pb exposure, as well as domestic utensils routinely used for feeding children.

The International Agency for Research on Cancer (IARC 1993) classifies Cd as a substance carcinogenic for humans whose childhood exposure is associated with adverse health effects in adult life, such as renal problems (Schoeters et al. 2006). Moreover, the United States Centers for Disease Control (CDC) has established a blood lead reference value of 5 µg.dL^{-1}, calculated according to the 97.5th percentile based on the National Health and Nutrition Examination Survey (NHANES) (CDC 2012). However, the toxic effects of lead can be seen in children at concentrations lower than this reference value. According to Paulson and Brown (2018), this value is in the process of being revised to the lower limit of 3.5 µg.dL^{-1}. Plastic utensils are one of many sources and routes of exposure for children. In a study of 50 day care centers with 2397 children, the authors found blood lead levels of around 2.16 µg.dL^{-1} and a 97.5th percentile of 13.9 µg.dL^{-1} (Olympio et al. 2015; Olympio et al. 2018). In a later investigation involving a subsample of the Olympio et al. (2018) study, Silva et al. (2018) explored potential sources of lead exposure, identifying sources that included paint coatings of walls, floors, doors, windows, as well as plastic toys and utensils handled by children at day care centers and within their homes. Other studies have investigated the associations of blood lead levels with exposure of children aged 1-4 years by analyzing 24h diet in school and household settings. The results showed Pb levels of 2.71 µg.dL^{-1} in blood, 1.61 – 2.24 µg.kg^{-1} in the diet, and bioaccessibility for Pb, Cd and As of 0.18 ± 0.11 µg.kg^{-1}, 0.08 ± 0.04 µg.kg^{-1} and 0.61± 0.41µg.kg^{-1}, respectively (Leroux et al. 2018a; Leroux et al. 2018b). In addition, another route of exposure to these metals occurs in the form of informal home-based work. For example, in the production of jewelry and fashion jewelry in the city of Limeira, São Paulo state, children or other members of the household are exposed to elements such as Pb, Cd, As, among others (Ferreira et al. 2019; Pereira et al. 2020; Salles et al. 2021).

Therefore, there is a clear need for further studies investigating plastic utensils for use by children as a source of exposure not only to Cd and Pb, but also to other PTEs these materials may contain. Moreover, as outlined previously, contamination of these materials by Cd and Pb is not a problem specific to Brazil, but an issue documented in many other countries including the USA, China and Kazakhstan (Guney and Zagury 2013; Kang and Zhu 2015; Cui et al. 2015; Turner 2018; Akimzhanova et al. 2020). In the present study, a large proportion of the plastic utensils tested were imported, predominantly from China, a major trading partner for Brazil.

Only the simulant solutions of water and acetic acid 3% (m/v) were employed in the present investigation. Official Brazilian guidelines recommend that, for fatty foodstuffs such as milk, ethanol-based solutions be used at the appropriate concentrations according to the type of food under analysis. It is important to point out, however, that the regulatory body states that the use of acetic acid 3% (m/v) as a simulant solution suffices for performing migration tests. Another important factor is the temperature at which experiments are conducted, where suggested temperatures are provided by the legislation and EN standards cited.

5. Conclusions

The Cd and Pb concentrations determined are cause for concern, given the vast majority of plastic utensils assessed contained levels exceeding permitted limits. Furthermore, the results of the migration tests evidenced the major potential bioaccessibility of these elements in foods and beverage, potentially leading to harmful health effects even at low levels. Thus, these colored plastic utensils represent a potential source of exposure to these contaminants.

Taken together, these results underscore the urgent need for stricter regulations and inspections governing the production of these materials, from the manufacturing process through to their use, where orange, yellow and green pigments were associated with the highest concentrations of Cd and Pb. Therefore, the use of colorless/transparent utensils is recommended as a means of mitigating exposure to these elements via this source, in that these elements are invariably employed to bind color to the plastic material.

As shown, the level of social vulnerability of the districts where utensils were purchased suggests a relationship between price and concentration of Cd and Pb in the utensils. However, it important to bear in mind shoppers tend to gravitate to commercial centers to buy these utensils and goods at low prices. Therefore, it stands to reason those locations which are a source of high concentrations of these elements may also pose a risk to populations living outside these districts.

Lastly, future studies systematically assessing other PTEs such as arsenic, a highly toxic substance with a range of health effects, using controlled migration tests are warranted. These other contaminants are also part of the WHO list of 10 chemicals of major public health concern.

Declarations

Ethics approval and consent to participate

Not applicable, as this study did not include people or animals.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Competing interests

The authors declare that they have no conflict of interest.

Funding

This research project was financially supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP. grant #2016/11087-8, #2016/10060-9. INL and ECP both received study scholarships (grants FAPESP #2017/14392-9 and #2014/20945-2).

Authors Contribution

Elizeu Chiodi Pereira and Isabelle Nogueira Leroux: conceptualization, fieldwork, chemical analyses, manuscript's writing and final editing.

Maciel Santos Luz and Bruno Batista Lemos: Chemical analyses supervision, funding, manuscript´s final editing.

Kelly Polido Kaneshiro Olympio: study's conceptualization and design, supervision, funding, manuscript's writing and final editing

Acknowledgements

The authors extend their thanks to the volunteer storeowners who made their outlets available for analysis of utensils in loco using XRF.

References

1. Advisory Committee on Childhood Lead Poisoning Prevention of the Centers for Disease Control and Prevention (2012) Low level Lead exposure harms children: a renewed call for primary prevention. US Department of Health and Human Services
2. Akimzhanova Z, Guney M, Kismelyeva S et al (2020) Contamination by eleven harmful elements in children's jewelry and toys from Central Asian market. Environ Sci Pollut Res 27:21071–21083. https://doi.org/10.1007/s11356-020-08631-5
3. Bellinger DC (2004) Lead Pediatrics 113:1016–1022
4. Blackowicz MJ, Hryhorczuk DO, Rankin KM et al (2016) The Impact of Low-Level Lead Toxicity on School Performance among Hispanic Subgroups in the Chicago Public Schools. Int J Environ Res Public Health. https://doi.org/10.3390/ijerph13080774
5. Brasil (2008) Lei nº 11.762, de 1º de agosto de 2008.Fixa o limite máximo de chumbo permitido na fabricação de tintas imobiliárias e de uso infantil e escolar, vernizes e materiais similares e dá outras

providências. Diário Oficial União. [Em Português]

6. Brasil (2010a) Resolução de Diretoria Colegiada – RDC Nº 51, de 26 de novembro de 2010. Dispõe sobre migração em materiais, embalagens e equipamentos plásticos destinados a entrar em contato com alimentos. Diário Oficial da União. [Em Português]
7. Brasil (2010b) Resolução de Diretoria Colegiada – RDC Nº 52, de 26 de novembro de 2010. Dispõe sobre corantes em embalagens e equipamentos plásticos destinados a estar em contato com alimentos. Diário Oficial da União. [Em Português]
8. Carvalho LVB et al (2017) Exposição ocupacional a substâncias químicas, fatores socioeconômicos e Saúde do Trabalhador: uma visão integrada. Saúde em Debate, v.41, n. esp.2, p.313-326, 2017. https://doi.org/10.1590/0103-11042017s226
9. Cui XY, Li SW, Zhang SJ, Fan YY, Ma LQ (2015) Toxic metals in children's toys and jewelry: coupling bioaccessibility with risk assessment. Environ Pollut. https://doi.org/10.1016/j.envpol.2015.01.035
10. Dickerson AS, Rahbar MH, Bakian AV et al (2016) Autism spectrum disorder prevalence and associations with air concentrations of lead, mercury, and arsenic. Environ Monit Assess. https://doi.org/10.1007/s10661-016-5405-1
11. Demont M, Boutakhrit K, Fekete V, Bolle F, Van Loco J (2012) Migration of 18 trace elements from ceramic food contact material: influence of pigment, pH, nature of acid and temperature. Food Chem Toxicol 50(3-4):734–743. https://doi.org/10.1016/j.fct.2011.12.043
12. EUROPEAN COMMITTEE FOR STANDARDIZATION (2002a) EN 1186-1: materials and articles in contact with foodstuffs – plastics. Part 1: guide to the selection of conditions and teste for overall migration. Brussels, 49 p
13. EUROPEAN COMMITTEE FOR STANDARDIZATION (2002b) EN 1186-3: materials and articles in contact with foodstuffs – plastics. Part 3: test methods for overall migration into aqueous food simulants buy total immersion. Brussels. 17 p
14. Ferrreira APSDS, Pereira EC, Salles FJ, Silva FFD, Batista BL, Handakas E, Olympio KPK (2019) Home-based and informal work exposes the families to high levels of potentially toxic elements. Chemosphere. https://doi.org/10.1016/j.chemosphere.2018.11.083
15. Greenway JA, Gerstenberger S (2010) An evaluation of lead contamination in plastic toys collected from day care centers in the Las Vegas Valley, Nevada, USA. Bull Environ Contam Toxicol. 2010 Oct;85(4):363-6. doi: https://doi.org/10.1007/s00128-010-0100-3
16. Hornung RW, Lanphear BP, Dietrich KN (2009) Age of greatest susceptibility to childhood lead exposure: a new statistical approach. Environ Health Perspect. https://doi.org/10.1289/ehp.0800426
17. Huzl F, Joachimsthaler J, Sykora J, Syblik J (1960) Lead poisoning in ceramic industry. Prac Lek. PMID: 14405678
18. IARC (1993) Cadmium and cádmium compounds. IARC Monogr Eval Carcing Risks Hum, 58: 119-237. PMID: 8022055
19. Inmetro (2015) Relatório de análise de chumbo em tintas. Inmetro. Rio de Janeiro, setembro de 2015. [Em Português]

20. Kang S, Zhu J (2015) Total lead content and its bioaccessibility in base materials of low-cost plastic toys bought on the Beijing market. J Mater Cycles Waste Manag 17:63–71. https://doi.org/10.1007/s10163-013-0223-9
21. Kiyataka PH, Dantas ST, Pallone JA (2014) Method for assessing lead, cadmium, mercury and arsenic in high-density polyethylene packaging and study of the migration into yoghurt and simulant. Food Addit Contam Part A Chem Anal Control Expo Risk Assess 31(1):156–163. https://doi.org/10.1080/19440049.2013.855826
22. Li Y, Hu J, Wu W, Liu S, Li M et al (2016) Application of IEUBK model in lead risk assessment of children aged 61–84 months old in central China. Sci Total Environ 541:673–682. https://doi.org/10.1016/j.scitotenv.2015.09.103.6
23. Mateus-García A, Ramos-Bonilla JP (2014) Presence of lead in paint of toys sold in stores of the formal market of Bogotá. Colombia Environ doi. https://doi.org/10.1016/j.envres.2013.11.005
24. Mazumdar M, Bellinger DC, Gregas M, Abanilla K, Bacic J, Needleman HL (2011) Low-level environmental lead exposure in childhood and adult intellectual function: a follow-up study. Environ Health. https://doi.org/10.1186/1476-069X-10-24
25. Mert Guney, Gerald J, Zagury (2013) Contamination by Ten Harmful Elements in Toys and Children's Jewelry Bought on the North American Market. Environmental Science Technology 47(11):5921–5930. https://doi.org/10.1021/es304969n
26. Needleman H. Lead poisoning (2004) Annu Rev Med. https://doi.org/10.1146/annurev.med.55.091902.103653
27. Lanphear BP et al (2005) Low-level environmental lead exposure and children's intellectual function: an international pooled analysis. Environmental health perspectives vol. 113,7 (2005): 894-9. https://doi.org/10.1289/ehp.7688
28. Leroux IN, Ferreira APSDS, Silva JPDR, Bezerra FF, da Silva FF, Salles FJ, Luz MS, de Assunção NA, Cardoso MRA, Olympio KPK (2018a) Lead exposure from households and school settings: influence of diet on blood lead levels. Environ Sci Pollut Res Int. https://doi.org/10.1007/s11356-018-3114-8
29. Leroux IN, Ferreira APSDS, Paniz FP, Pedron T, Salles FJ, da Silva FF, Maltez HF, Batista BL, Olympio KPK (2018b) Lead, Cadmium, and Arsenic Bioaccessibility of 24 h Duplicate Diet Ingested by Preschool Children Attending Day Care Centers in Brazil. Int J Environ Res Public Health. https://doi.org/10.3390/ijerph15081778
30. Magna GAM, Machado SL, Portella RB, Carvalho MF (2014) Avaliação da exposição ao Pb e Cd em crianças de 0 a 17 anos por consumo de alimentos vegetais cultivados em solos contaminados no município de Santo Amaro (BA). Eng. Sanit. Ambient. vol.19, n.spe, pp.3-12. https://doi.org/10.1590/S1413-41522014019010000430. [Em Português]
31. Mateus-García A, Ramos-Bonilla JP (2014) Presence of lead in paint of toys sold in stores of the formal market of Bogotá, Colombia. Environ Res. https://doi/10.1016/j.envres.2013.11.005
32. Olympio KPK, Gonçalves C, Günther WM, Bechara EJ (2009) Neurotoxicity and aggressiveness triggered by low-level lead in children: a review. Rev Panam Salud Publica Sep 26(3):266–275.

https://doi.org/10.1590/s1020-49892009000900011

33. Olympio KPK, Oliveira PV, Naozuka J, Cardoso MR, Marques AF, Günther WM, Bechara EJ (2010) Surface dental enamel lead levels and antisocial behavior in Brazilian adolescents. Neurotoxicol Teratol Mar-Apr 32(2):273–279. https://doi.org/10.1016/j.ntt.2009.12.003
34. Olympio KPK, Barbosa F, Silva AS, Cardoso MRA (2015) Lead exposure in São Paulo, Brazil: blood levels and risk factors associated. In: 54th Annual Meeting and Tox Expo, San Diego, California, EUA. The Toxicologist - Supplement to Toxicological Sciences, vol. 144. Oxford University Press, pp. 104e105
35. Olympio KPK, Gonçalves CG, Salles FJ, Ferreira AP, Soares AS, Buzalaf MA, Cardoso MR, Bechara EJ (2017) What are the blood lead levels of children living in Latin America and the Caribbean? Environ Int Apr 101:46–58. https://doi.org/10.1016/j.envint.2016.12.022
36. Olympio KPK, Silva JPR, Silva AS et al. (2018)Blood lead and cadmium levels in preschool children and associated risk factors in São Paulo, Brazil. Environmental Pollution, Volume 240, Pages 831–838. https://doi.org/10.1016/j.envpol.2018.04.124
37. OSHA Brief - Medical Evaluation of Renal Effects of Cadmium Exposures. Disponível em: < https://www.osha.gov/cadmium/health-effects>. Acesso 07 de julho de 2021.
38. Paulson JA, Brown MJ (2019) The CDC blood lead reference value for children: time for a change. Environ Health 18:16. https://doi.org/10.1186/s12940-019-0457-7
39. Pereira EC, Ferreira APS, Sato APS et al (2020) Home-based outsourced informal work by children and adolescents impacts sleep and leisure—a preliminary study. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-020-09551-0
40. Rafati Rahimzadeh M, Rafati Rahimzadeh M, Kazemi S, Moghadamnia AA (2017) Cadmium toxicity and treatment: An update. Caspian J Intern Med. https://doi.org/10.22088/cjim.8.3.135
41. Salles FJ, Tavares DJB, Freira BM, Ferreira APSS, Handakas E, Batista BL, Olympio KPK (2021) Home-based informal jewelry production increases exposure of working families to cádmium. Science of The Total Environment. https://doi.org/10.1016/j.scitotenv.2021.147297
42. Silva JPR et al (2018) High blood lead levels are associated with lead concentrations in households and day care centers attended by Brazilian preschool children. Environmental pollution. https://doi.org/10.1016/j.envpol.2018.04.080
43. Schoeters G, Den HE, Zuurbier M, Naginiene R et al (2006) Cadmium and children: exposure and health effects. Acta Paediatr Suppl Oct 95(453):50–54. https://doi.org/10.1080/08035320600886232
44. Tamayo y Ortiz M, Téllez-Rojo MM, Hu H, Hernández-Ávila M et al (2016) Lead in candy consumed and blood lead levels of children living in Mexico City. Environ Res May 147:497–502. https://doi.org/10.1016/j.envres.2016.03.007
45. Turner A (2018) Concentrations and Migratabilities of Hazardous Elements in Second-Hand children’s Plastic toys. Environmental Science Technology 52(5):3110–3116. https://doi.org/10.1021/acs.est.7b04685

46. U.S. Consumer Product Safety Commission (1997) CPSC Staff Report on Lead and Cadmium in Children's Polyvinyl Chloride (PVC) Products. Washington DC. Available in: https://www.cpsc.gov/content/cpsc-staff-report-lead-and-cadmium-childrens-polyvinyl-chloride-pvc-products (accessed 10 jun 2021)
47. Wagner PJ, Park HR, Wang Z et al (2017) In Vitro Effects of Lead on Gene Expression in Neural Stem Cells and Associations between Up-regulated Genes and Cognitive Scores in Children. Environ Health Perspect. https://doi.org/10.1289/EHP265
48. Whitt M, Brown W, Danes JE, Vorst KL (2016) Migration of heavy metals from recycled polyethylene terephthalate during storage and microwave heating. Journal of Plastic Film Sheeting 32(2):189–207. https://doi.org/10.1177/8756087915590190
49. World Health Organization (WHO). Childhood Lead Poisoning. World Health Organization, Geneva, Switzerland (2011) Available in: http://www.who.int/ceh/publications/leadguidance.pdf (accessed 10 jun 2021)

Figures

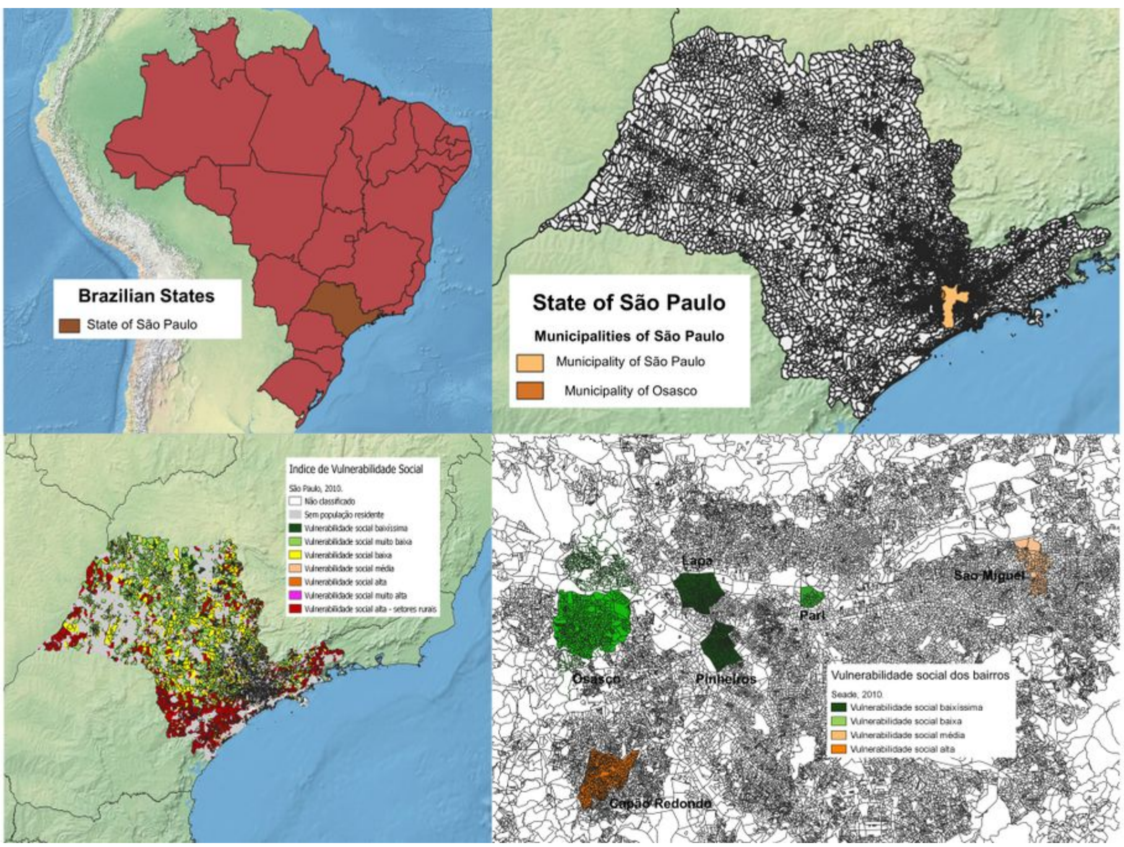

Figure 1

Distribution of IPVS for districts where utensils were purchased.