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Title: Chemical safety of children's play paints: focus on selected heavy metals

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Abstract: Children's play paints are widely used as didactic products in preschool activities. Besides direct skin contact, a great risk of oral exposure exists during its normal and foreseeable use. Due to the ubiquitous nature of most metals, their presence as impurities in all products is recognized as unavoidable. However, the toxic potential of most of them requires that their levels are kept as low as possible.

The present study aimed to assess the content of selected heavy metals (Pb, Cd, Cr, Co, Ni, Mn, Cu and Zn) in "artist paints" (n=54) and "face paints" (n=12) commonly used in preschool establishments and available at low cost stores. Determinations were carried out by GFAAS (for Pb, Cd, Co, Cr and Ni) and FAAS (for Mn, Cu and Zn).

The levels obtained [mean±SD (maximum)] were: 0.48±0.44 (1.98) µg g-1 for Pb; 0.04±0.04 (0.30) µg g-1 for Cd; 0.17±0.20 (1.47) µg g-1 for Co; 1.36±2.18 (9.40) µg g-1 for Cr; 0.63±0.56 (3.10) µg g-1 for Ni; 19.8±88.2 (718) µg g-1 for Mn; 108±260 (1458) µg g-1 for Cu; 130±564 (3478) µg g-1 for Zn.

A safety assessment considering the estimated potential exposure and health-based limits (tolerable daily intakes) was performed. Overall, the results showed no reasons for safety concerns regarding the studied elements.

Dear Editor,

I am submitting the article titled: “Chemical safety of children’s play paints: focus on selected heavy metals” for publication in Microchemical Journal.

The corresponding author of this article is Edgar Pinto. The address is Rua Valente Perfeito, 322, 4400-330, Vila Nova de Gaia, Portugal, Portugal; Tel: +351 222 061 000; Fax: +351 222 061 001; Email: ecp@estsp.ipp.pt.

Looking forward that it is accepted for publication.

Best regards

Edgar Pinto

Response to reviewers' comments

Reviewers' main comment: *The paper presents a study about the levels of metals in different types of toys, and their possible toxic effects on children. The aim of the paper is interesting but my principal objection is that the number of samples studied are very short in order to obtain a general conclusion. About the analytical method there is not nothing new, the only new is the samples analyzed, then it is necessary a bigger samples number before the acceptation of the paper.*

- The authors agree with reviewers about the number of samples analyzed. We add 35 more samples, now reaching a total of 66 paints analyzed regarding their metal content. It is fully representative of the Portuguese market. A new type of paint was also included (fingerpaint) in order to give more relevance and comprehensiveness to the study.

1 - More information about the quality control of the results must be enclosed, for example, what type of Certified Reference Material was used to check the accuracy of the methods?

- (Lines 133-138) A new section was introduced "*2.3 Quality Control*" and the results from the analysis of the certified reference material ISE918 (sandy soil) are presented in a new table (Table 1).

2 - What about the blank values?

- (Lines 145-147) A new sentence was included to address the question of blank values: "In each batch of microwave-assisted acid digestion (i.e., 10 vessels) one sample blank was included. In total, 23 sample blanks were performed. The obtained mean values were subtracted from the sample values."

3 - Had you problems about matrix effects?

- (Lines 139-144) A new sentence was included to clarify how the evaluation of matrix effects was carried out: "The effect of the sample matrix on the accuracy of the analytical determinations was assessed through a matrix-matched calibration approach. Standard solutions were added to the matrix (i.e., paint), calibration curves were built and slopes were compared with those obtained for simple aqueous standard solutions. No significant differences ($p > 0.05$) were observed between the obtained slopes. Thus, the analytical procedures were considered free from matrix effects."

4 - Why the number of samples is low?, authors say in the conclusion section, lines 348-352, that it is not possible to obtain a general conclusion because the number of samples is low and then that more work is necessary. Can you explain then why did not include more samples?

- (Lines 362-375) The samples analyzed were representative of the main products and brands found in the Portuguese market and preschool establishments. However, as abovementioned, more samples were analyzed. The conclusion section was rewrite to demonstrate the main achievements of the present study: "The data obtained in this study provide useful information about the content of selected heavy metals in children paints and related potential risk of exposure to these elements. In general, the content of heavy metals in the studied samples were well below the migrations limits set by the TSD and levels (for Pb and Cd) considered as technically achievable for cosmetics using good manufacturing practices. However, given the fact that the content of heavy metals in finished products strongly depends on the quality of raw-materials and manufacturing process, it is difficult to extrapolate to other contexts (other lots, other brands, other countries/markets). Therefore, further studies and periodic monitoring are needed for a full safety characterization of this kind of products. The differences in metal content between the different categories of paints are related with manufacturing processes and their specific composition. However, it was not possible to associate the higher metal levels with specific ingredients, particularly pigments, since these products do not have label information about its composition."

Highlights

- Heavy metals can be present in children's play paints due to their ubiquitous and persistent nature.
- Eight heavy metals (Pb, Cd, Cr, Co, Ni, Mn, Cu and Zn) were determined in several products types, colors, brands and country of manufacture.
- Overall, the results showed no reasons for safety concerns regarding the studied elements
- Heavy metals in finished products strongly depends on the quality of raw-materials and manufacturing process
- A close monitoring is needed for a full safety characterization of this kind of products

Chemical safety of children's play paints: focus on selected heavy metals

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Abstract

Children's play paints are widely used as didactic products in preschool activities. Besides direct skin contact, a great risk of oral exposure exists during its normal and foreseeable use. Due to the ubiquitous nature of most metals, their presence as impurities in all products is recognized as unavoidable. However, the toxic potential of most of them requires that their levels are kept as low as possible.

The present study aimed to assess the content of selected heavy metals (Pb, Cd, Cr, Co, Ni, Mn, Cu and Zn) in "artist paints" (n=54) and "face paints" (n=12) commonly used in preschool establishments and available at low cost stores. Determinations were carried out by GFAAS (for Pb, Cd, Co, Cr and Ni) and FAAS (for Mn, Cu and Zn).

The levels obtained [mean±SD (maximum)] were: 0.48±0.44 (1.98) µg g^{-1} for Pb; 0.04±0.04 (0.30) µg g^{-1} for Cd; 0.17±0.20 (1.47) µg g^{-1} for Co; 1.36±2.18 (9.40) µg g^{-1} for Cr; 0.63±0.56 (3.10) µg g^{-1} for Ni; 19.8±88.2 (718) µg g^{-1} for Mn; 108±260 (1458) µg g^{-1} for Cu; 130±564 (3478) µg g^{-1} for Zn.

A safety assessment considering the estimated potential exposure and health-based limits (tolerable daily intakes) was performed. Overall, the results showed no reasons for safety concerns regarding the studied elements.

Keywords: toys, children, artist paints, face paints, heavy metals

1. Introduction

In early childhood education, activities such as drawing and painting help children to develop self-expression skills, and significantly contribute to their physical and psychological development [1]. According to Arda [2], painting is a stronger form of expression than words in early years, which makes play paints an attractive tool for preschool activities. These paints can be divided into two main groups: "artist paints" (e.g., gouaches, watercolors, acrylic paints) and the "face paints".

Given its purpose, *artist paints* fall within the concept of toy («a product designed or intended, whether or not exclusively, for use in play by children under 14 years of age») and their safety in the European Union is regulated under the Directive 2009/48/EC on the safety of toys (hereinafter the "Toy Safety Directive" will be designated as TSD) [3]. This category of toys is susceptible of easy ingestion in significant quantities and they should comply with maximum acceptable levels for the migration of toxic elements [4]. Metals may be released from toys by different mechanisms such as the action of saliva during mouthing, sweat during dermal contact or gastric fluid after ingestion [5]. Therefore, high amounts of metals may become bioavailable, reach the systemic circulation and exert their toxicological effects on target organs. Severity of the exposure depends on the content, physiological parameters, behavioral patterns and bioavailability of the metal [5]. The TSD lays down migration limits for 18 different elements, including the heavy metals Pb, Cd, Co, Cr, Ni, Mn, Cu and Zn.

As regards to *face paints*, they have to be considered as cosmetic products [«any substance or mixture intended to be placed in contact with the external parts of the human body (…) with a view exclusively or mainly to (...) changing their appearance…»], according to the EU Regulation (EC) no. 1223/2009 on cosmetics products (hereinafter "Cosmetics Regulation") [6]. The Cosmetics Regulation states that "products should be safe under normal or reasonable foreseeable conditions of use. In particular, a risk-benefit reasoning should not justify a risk to human health" [6]. Children's face paints are directly applied to skin, and mainly produce local exposure to ingredients. However, the use of these products by children is of particular concern mainly because of the potential for exposure through ingestion [7].

The dermal contact with chemical substances, natural or synthetic, will always involve some risk of irritation and sensitization (particularly allergic contact dermatitis) [8-10]. Although topical exposure usually does not result in significant penetration through the skin, the human systemic exposure can rarely be completely excluded [8]. The risk of percutaneous absorption is variable depending on the site of application of the product (e.g., products applied directly to mucous membranes pose a greater risk). When children play with paints, skin contact and potential absorption through the skin is almost unavoidable.

Due to their ubiquitous and persistent nature, the presence of metals as impurities in all products is recognized as unavoidable (trace amounts arising from both the ingredients and manufacturing practices) [11]. However, for safety reasons, their levels should be kept at the lowest levels that are technically feasible or are of no toxicological concern.

Based on this background, the aim of our work was to determine the content of Pb, Cd, Cr (total), Co, Ni, Mn, Cu and Zn in artist paints and face paints used by children in preschool establishments and widely available in low cost stores. Results were compared with legal limits and values obtained in similar studies. It was also evaluated whether there were significant differences between metals content in the different types of products (gouaches, acrylics, watercolors, fingerpaints and face paints). In order to assess the safety of the products, the potential metal intake was evaluated and compared with tolerable daily intakes.

2. Material and methods

2.1. Sample collection

Using a convenience sampling procedure, samples of artist paints (n=54) and face paints (n=12) were collected in 8 preschool establishments (20 products) and purchased in 7 low cost stores (46 products) from Porto (Portugal). All the selected paints were specifically designed for children use, representing 17 popular brands. The paints collected in preschool establishments were mainly used by children aged between 3 and 6 years old. The general information about the samples (brand, type, color and country of manufacture) and the local of acquisition (school or store) is provided in Table 2. An identification code consisting of a combination of a letter and a number was assigned to each sample. For the artist paints the letters indicate the type of product: G-gouache; A-acrylic; W-watercolor; FP-fingerpaint. Face paints are indicated by the letter “F”. The brand is also indicated by a code consisting of a combination of a letter (“B”, for brand) and a number. A different number was attributed to each sampling site too.

2.2. Sample analysis

The samples were solubilized by closed-vessel microwave-assisted acid digestion in a MLS-1200 Mega (Sorisole, Italy) microwave oven equipped with an HPR-1000/10 S rotor. A sample mass between 0.3-0.5 g was directly weighted into the microwave oven polytetrafluorethylene (PTFE) vessels and 4 mL of high-purity concentrated nitric acid (HNO_3) (65% w/w, *Trace*SELECT® Ultra, from Fluka, L’Isle d'Abeau Chesnes, France) plus 1 mL of high-purity hydrogen peroxide (H_2O_2) (30% v/v, *Trace*SELECT®, from Fluka, Seelze, Germany) was added. Then, the sample digestion was performed using the following microwave oven program (power [W]/time [min]): 250/2, 0/2, 600/5, 500/5, 400/5. After cooling, sample solutions were transferred into a 50 mL decontaminated polypropylene volumetric flask and the volume was adjusted with ultra-pure water (> 18.2 MΩ.cm at 25 ºC) obtained from a Milli-Q (Millipore, Billerica, MA) RG water purification system. Sample blanks were obtained using the same procedure. The obtained solutions (blanks and digested samples) were stored in tightly closed decontaminated polypropylene tubes in the refrigerator at 4 ºC until analysis.

Each sample was analyzed in triplicate. The metals determinations were carried out using graphite furnace atomic absorption spectrometry (GFAAS) for Pb, Cd, Co, Cr and Ni, and flame-atomic absorption spectrometry (FAAS) for Mn, Cu and Zn.

For GFAAS determinations, a Perkin Elmer (Überlingen, Germany) model 4100 ZL instrument (longitudinal Zeeman-effect background correction), equipped with a transverse heated graphite atomizer (THGA) and an AS-70 auto-sampler was used. For FAAS determinations, a Perkin Elmer model 3100 instrument (air/acetylene flame) was used. Calibration standards were prepared by adequate dilution with HNO_3 0.2% (v/v) of a multi-element (Pb, Cd, Co, Cr, Ni, Mn, Cu and Zn) standard stock solution. This was prepared from single-element 1000 mg L^{-1} commercial standard solutions (Sigma, St. Louis, MO). The limits of detection (LoD) were calculated as the concentration corresponding to 3 times the standard deviation of a series of 10 replicate measurements of the calibration blank (HNO_3 0.2% v/v).

2.3 Quality Control

Since paints are not available as a certified reference material (CRM) for metal analysis, a sandy soil (ISE 918) supplied by WEPAL (Wageningen, The Netherlands) was used for analytical quality control purposes. The CRM was subjected to the same sample pretreatment as the studied paints. The values obtained proved the adequacy of the analytical procedure (Table 1).

The effect of the sample matrix on the accuracy of the analytical determinations was assessed through a matrix-matched calibration approach. Standard solutions were added to the matrix (i.e., paint), calibration curves were built and slopes were compared with those obtained for simple aqueous standard solutions. No significant differences ($p > 0.05$) were observed between the obtained slopes. Thus, the analytical procedures were considered free from matrix effects.

In each batch of microwave-assisted acid digestion (i.e., 10 vessels) one sample blank was included. In total, 23 sample blanks were performed. The obtained mean values were subtracted from the sample values.

2.4. Data analysis

Statistical analysis was performed using IBM (New York, NY) SPSS Statistics 20 software. For the statistics calculation, results that fall below the LoD were assumed as the LoD divided by the square root of 2, a commonly used procedure for data imputation [12]. Descriptive statistics was used to summarize the results for artist paints and face paints separately. Student's t-test was performed to evaluate the matrix effects. The difference in metal content between the different types of paints was tested with the non-parametric Kruskal-Wallis test followed by a multi comparison analysis using the Dunnet's T3 test. Statistical significance was considered for $p < 0.05$.

2.5. Safety assessment

Measured metals content was used to assess the safety of the products using the methodology for assessment of chemical safety of toys, option 2 (use of product composition data), as proposed by the National Institute for Public Health and the Environment (RIVM) [13]. The exposure scenario considered was the direct ingestion, mostly associated to hand-to-mouth (HTM) contact. Hand-to-mouth contact is a child specific behavior that can lead to a relevant exposure [14], especially in children under 3 years of age. This methodology is based on the calculation of the amount of element released from the estimated amount of product ingested, i.e., the estimated daily intake (EDI) divided by the mean body weight of the children. This value should be lower than a defined fraction (usually 5, 10 or 20%) of the tolerable daily intake (TDI, in mg kg^{-1} bw day^{-1}) for the element of interest [13]. This is a two-step calculation that involves:

1) Calculation of the EDI, as follows:

$$EDI\ (\mu g/kg\ bw/day) = \frac{element\ content\ in\ product\ (\mu g/g) \times weight\ of\ product\ ingested\ (g/day)}{body\ weight\ (kg)}$$

For this purpose, it was assumed that the maximum daily intake of artist paints and face paints (i.e., the maximum amount of product that can be ingested by children) is 400 mg day^{-1} and 210 mg day^{-1}, respectively, as proposed by RIVM [13,14], and the total amount of the element in the product is released at once and becomes readily available for gastrointestinal absorption (i.e., bioaccessibility is 100%). The children body weight was set at 12 kg, as proposed by EFSA (a default value for children under 3 years old) [15].

2) Calculation of the relative intake indices (RII), as follows:

$$RII\ (\%) = \frac{EDI}{TDI} \times 100$$

3. Results and discussion

A total of 66 samples were analyzed, 54 artist paints and 12 face paints, representing 17 different brands (see Table 2). All the products had a package label providing information about the product and country of manufacture. China was the predominant country of origin (42.4%), followed by Italy (28.8%), France (15.2%), UK (10.6%) and Spain (3.0%). The samples purchased in low cost stores were mostly from China (58.7%). Watercolors were the most available artist paint, representing the highest percentage of the samples analyzed (34.8%), followed by gouaches (30.3%), face paints (18.2%), fingerpaints (9.1%) and acrylics (7.6%). The colors most analyzed were yellow (16.7%), red (15.2%), and white and green (13.6% each).

The results of metal content in the studied products are summarized in Table 3. Considering that artist paints and face paints are covered by different regulations (toys and cosmetics, respectively), data analysis was performed separately. It must be noted that the total element content was determined by performing a complete solubilization (microwave-assisted acid digestion) of the samples, a different extraction procedure from that described in the standard for the determination of migration limits, which simply simulates the material contact with the stomach acid for a defined period of time after swallowing. Results obtained therefore represent what may be considered as the worst case scenario regarding the exposure to the elements.

3.1. Metal content in artist paints

The average content of Pb in artist paints (gouaches, acrylics, watercolors and fingerpaints) was 0.52±0.48 µg g^{-1}. Gouaches presented the highest content of Pb (0.65±0.48 µg g^{-1}) while fingerpaints presented the lowest (all results were below the LOD), a significant statistical difference. The migration limit for Pb set by the TSD (3.4 µg g^{-1}) was not exceeded in any of the samples analyzed, even assuming that the total Pb content is susceptible to be released. Germany continues to apply, provisionally, its own national limits for certain heavy metals in toys, including Pb, which are stricter than the EU standards, defining a maximum daily bioavailability of 0.7 µg for Pb [16]. As regards the requirements in countries outside de EU, the Canadian Hazardous Products Act limits to 90 µg g^{-1} the total content of Pb in surface coating materials of toys for children younger than 3 years old [17]. Similarly, in the USA, the Consumer Product Safety Improvement Act (CPSIA) of 2008 also sets the concentration of Pb in paint to a limit of 90 µg g^{-1} [18].

Cadmium presented the lowest average content among the studied metals: 0.04±0.05 µg g^{-1}. The highest levels were found in gouaches (0.05±0.07 µg g^{-1}) and the lowest in fingerpaints (0.02±0.01 µg g^{-1}). None of the samples exceeded the migration limit imposed by the TSD (0.5 µg g^{-1}).

For the transitions metals Cr, Co and Ni, the average content in artist paints was 1.36±2.64 µg g^{-1}, 0.17±0.22 µg g^{-1} and 0.69±0.55 µg g^{-1}, respectively. The highest Cr levels were found in watercolors (2.43±3.28 µg g^{-1}), which were significantly higher than the levels in fingerpaints. Five of the samples presenting the highest values (W_{28}, W_{29}, W_{30}, W_{31} and W_{32}) were purchased in low cost stores, with maximum Cr content reaching 9.4 µg g^{-1}. The TSD sets different migration limits to Cr(III) and Cr(VI): 9.4 µg g^{-1} and 0.005 µg g^{-1}, respectively. Therefore, no definite conclusion can be drawn, because our value corresponds to the total Cr content. For Co and Ni, none of the artist paints has exceeded the migration limits set by the TSD: 2.6 µg g^{-1} for Co and 18.8 µg g^{-1} for Ni.

As regards Mn, the mean content was 9.65±14.38 µg g^{-1}. Gouaches presented a significantly higher content (20.5±19.4 µg g^{-1}) than other artist paints. However, none of the samples reached the TSD migration limit of 300 µg g^{-1}.

Copper was present at very different levels, with 12 samples (G_1, G_{13}, G_{15}, G_{17}, G_{20}, A_{21}, W_{31}, W_{32}, W_{36}, W_{42}, FP_{50} and FP_{54}) exceeding the TSD migration limit (156 µg g-

^{1}). The same was observed for Zn, with two samples (A_{23} and A_{25}) also exceeding the migration limit (938 µg g^{-1}). The average content of these elements in artist paints was 131±283 µg g^{-1} for Cu and 156±621 µg g^{-1} for Zn. However, it is worth mentioning again that these values correspond to the total content in the product and not the actual content susceptible to migration.

3.2. Metal content in face paints

The average content of Pb in face paints (0.29±0.17 µg g^{-1}) was quite similar to the results obtained in the CSC study [19] on children's face paints of the USA market, with Pb levels ranging from 0.054 µg g^{-1} to 0.65 µg g^{-1}. Several studies had also determined the Pb content in other cosmetic products, mainly in eye shadows and lip products [20-23]. In a large survey of the US market (n=400 lipsticks), a mean Pb content of 1.11 µg g^{-1} (maximum 7.19 µg g^{-1}) was found [21]. Recently, the European Commission's Joint Research Centre conducted a survey of the Pb content in lip products of the European market (products purchased 15 different EU countries), and a mean Pb content of 0.75±0.64 µg g^{-1} was found (maximum 3.75 µg g^{-1}) [23].

According to the Cosmetics Regulation, Pb and its compounds are substances prohibited in cosmetic products. Nevertheless, trace amounts of this and other heavy metals are unavoidably found as impurities in all the products due to the persistent nature of these elements and the fact that they are found in the natural environment [24]. There are currently no international standards for impurities in cosmetics. The German authorities conducted studies to determine the background levels of heavy metal in cosmetic products, including toothpaste. Based on these studies, it was set that levels of Pb in cosmetic products above 20 µg g^{-1} were technically avoidable [25]. For toothpastes the maximum concentration was set at 1 µg g^{-1}. Health Canada, the federal department responsible for public health, considers that Pb levels in cosmetic products lower than 10 µg g^{-1} is technically feasible. Although these limits were based on levels that can be technically avoided and not in a risk-based approach [26], it is considered that they provide a high level of protection to susceptible subpopulations of consumers (namely children) when weighted against established tolerable intakes for this metal [24]. In our study, none of the samples exceeded this "limit" (10 µg g^{-1}).

Cadmium and its compounds are also forbidden in cosmetic products in EU [6]. The average content of Cd was 0.02±0.02 µg g^{-1}, well below the limits set by Health Canada (3 µg g^{-1}) and German authorities (5 µg g^{-1}) for this element in cosmetics. Similar results have been obtained in others studies regarding Cd in eye shadows and lip products [20,22].

For the transitions metals Co and Ni, the content in face paints was typically lower than 1 µg g^{-1}, a recommended limit value in consumer products for very sensitive individuals [27]. Chromium exceeded this value in 6 samples. Copper content was below the LoD in all the analyzed face paints. As regards Mn and Zn, the average content was 65.6±205.5 µg g^{-1} and 15.4±42.5 µg g^{-1}, respectively. The maximum Mn content was found in the sample F_{66} (717 µg g^{-1}) while the maximum Zn content was found in the same sample F_{58} (149 µg g^{-1}). Several Zn compounds are allowed in cosmetic products, mainly as white coloring agents, and others are allowed with some restrictions laid down in Cosmetic Regulation [e.g., $Zn(C_2H_3O_2)_2$ and $ZnCl_2$ are water-soluble zinc salts allowed in cosmetic products but restricted to a maximum concentration of 1% in ready for use preparations].

3.3. Safety assessment

The metal content determined in the studied samples (Table 3) was used for a safety assessment of the products. We used the methodology proposed by RIVM, option 2, which involves the use of product composition data [13] (for details, see Material and Methods section). The estimated daily intake was calculated assuming 400 mg day^{-1} (210 mg day^{-1} for face paints) as the amount of product ingested by the children. Data from RIVM [13] were used as tolerable daily intake (Table 4). A relative intake index (RII) for each element was calculated. This represents the fraction of the tolerable daily intake corresponding to the amount of metal ingested from the exposure to the products. Results are summarized in Table 5.

Lead and Cadmium – Pb and Cd are two highly toxic metals. The main route of Pb exposure is through the gastrointestinal tract. Children are particularly susceptible, since they absorb a higher amount of Pb than adults (up to 50% of ingested amount *versus* 10% in adults) [28]. Lead can also enter the body through dermal absorption, although this is less significant [28]. However, the cutaneous absorption of Pb may be increased when the skin is damaged (by scratches and wounds, for example). Under conditions of continued exposure, not all the Pb entering the body will be eliminated, and this results in accumulation in body tissues, especially in the bone [28]. The exposure to low levels of Pb in children is common and is particularly insidious because of the lack of diagnostically definitive physical signs [29]. Even at very low blood levels (5 μg dL^{-1} and even lower), Pb can result in neurotoxic effects and lasting effects on neurobehavioral functioning in children [29,30].

Cadmium accumulates in the human body, especially in the kidneys [31]. However, there is still limited data on the renal toxicity of Cd in children [32]. Since this is a cumulative element (Cd has a very long biological half-time), children exposure, even at very low levels, may have long-term adverse consequences [32], particularly in the nervous system, such as learning disabilities and hyperactivity [20]. Data from Table 5 shows that exposure to Pb and Cd resulting from the exposure to the studied products is very low (RII: 0.42±0.42% and 0.23±0.30%, respectively), with a RII lower than 2% in the worst case.

Nickel, chromium and cobalt – These transition metals are among the most common contact sensitizing chemicals (Table 4). Some authors have proposed that consumer products must contain less than 5 µg g^{-1} of Ni, Cr and Co, or preferably less than 1 µg g^{-1}, in order to minimize the risk for very sensitive individuals [27]. Table 6 shows the number of samples containing Cr, Co and Ni above 5 µg g^{-1}, between 1 µg g^{-1} and 5 µg g^{-1} and below 1 µg g^{-1}. The threshold of 1 µg g^{-1} was only exceeded for Ni, Cr and Co in 9, 16 and 1 samples, respectively. The threshold of 5 µg g^{-1} was only exceeded in 5 watercolor samples, which showed Cr contents between 7.4 and 9.4 µg g^{-1}. Samples purchased in low cost stores showed the worst results.

Nickel and its water soluble salts are of particular concern. Following sensitization, dermal exposure to even small amounts of Ni can cause outbreaks of dermatitis [33]. According to ATSDR, approximately 10-20% of the population is sensitive to Ni, developing dermal problems, even when exposed to low concentrations, either by ingestion or skin contact [34]. A Ni mass loading of 0.5 µg per cm^2 of skin area has been suggested as a no-effect level for sensitization, based on a wide range of studies [35]. According to RIVM [36], an exposure of about 3 mg/cm^2 of skin surface may be assumed as typical for face paint use. Thus, even in the *worst scenario* (i.e., for the maximum Ni level found: 3.10 µg g^{-1}), the exposure to Ni would represent only about 0.0093 $\mu g/cm^2$, approximately 50 fold lower than the no-effect level of 0.5 $\mu g/cm^2$, suggesting that an important margin of safety exists.

The chemical and toxicological properties of Cr are very different depending on the valence state of the element, Cr(VI) presenting a much higher toxicity than Cr(III), which is even an essential trace element [37]. As abovementioned, some people are very sensitive to dermal exposure Cr. In this study, no speciation analysis was carried out. However, even assuming that all the Cr present in the samples was Cr(VI), and taking into account only the non-carcinogenic effects by Cr(VI), very low RII (0.83±1.43%; maximum 6.27%) were obtained. For Co and Ni, RII were 0.37±0.49% (maximum 3.50%) and 0.20±0.18% (maximum 1.03%).

Manganese, copper and zinc – In adequate amounts, Mn is an essential nutrient for humans, however, in excessive concentrations it becomes a very toxic element [38,39]. Some authors have associated the exposure to high levels of Mn with hyperactivity and a decrease of development and intellectual function in children [38,40], like the ability of learn and remember [41]. *In vitro* studies suggest that Cu is poorly absorbed through intact skin [42], though some Cu compounds appear to be better absorbed than others. In addition, a very small percentage of infants and children are unusually sensitive to Cu [42]. Zn plays an important role in the growth and development of children. However, in excessive amounts it can also adversely affect human health. The ingestion of large doses of Zn (10-15 times higher than the Recommended Dietary Allowance – RDA), even for a short period, can cause stomach cramps, nausea and vomiting [43]. Furthermore, studies in animals indicate that low levels of certain Zn compounds (e.g., $Zn(C_2H_3O_2)_2$ and $ZnCl_2$) can cause skin irritation [43].

The results obtained show that for most samples the exposure to Mn, Cu and Zn is low (Table 5), with a RII 0.29±0.98% (max 7.85%) for Mn, and lower than 5% in 53/66 samples for Cu and 64/66 for Zn. The main exception was one acrylic paint (A_{21})

purchased in a low cost store, for which the estimated Cu intake was more than half the TDI (RII = 58.6%).

4. Conclusions

The data obtained in this study provide useful information about the content of selected heavy metals in children paints and related potential risk of exposure to these elements. In general, the content of heavy metals in the studied samples were well below the migrations limits set by the TSD and levels (for Pb and Cd) considered as technically achievable for cosmetics using good manufacturing practices. However, given the fact that the content of heavy metals in finished products strongly depends on the quality of raw-materials and manufacturing process, it is difficult to extrapolate to other contexts (other lots, other brands, other countries/markets). Therefore, further studies and periodic monitoring are needed for a full safety characterization of this kind of products. The differences in metal content between the different categories of paints are related with manufacturing processes and their specific composition. However, it was not possible to associate the higher metal levels with specific ingredients, particularly pigments, since these products do not have label information about its composition.

Figure Caption

Fig. 1. Box and whiskers plot showing the distributions of the metals content. Corresponding numeric data are provided in Table 3 for all samples (n = 66). Boxes extend from the 25th to the 75th percentile, horizontal bars inside the boxes represent the median, whiskers extend to maximum and minimum observations within 2 times the length of the interquartile range above and below the 75th and 25th percentiles, respectively, and outliers are represented as rhombus.

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Figure 1

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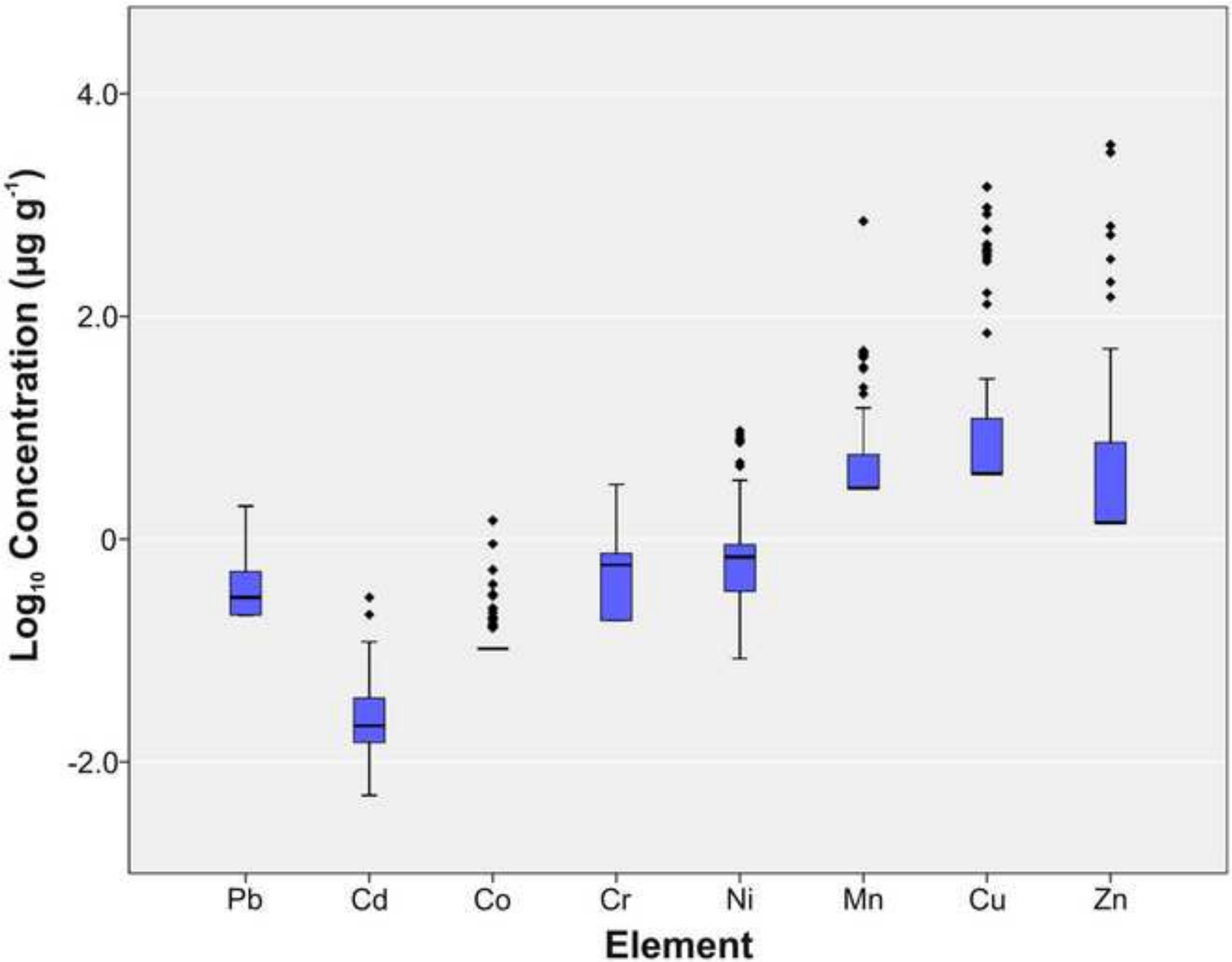

Table 1

Table 1 – Results obtained from the CRM (sandy soil) analysis (mean ± SD; n = 3).

Element	Certified value (μg g^{-1})	Analytical value (μg g^{-1})	Recovery (%)
Cd	0.250 ± 0.030	0.237 ± 0.016	94.8 ± 6.4
Co	1.25 ± 0.20	1.23 ± 0.04	98.5 ± 3.3
Cr	25.3 ± 3.0	24.0 ± 0.8	95.0 ± 3.1
Cu	16.8 ± 0.8	16.0 ± 0.3	94.2 ± 4.7
Mn	173 ± 12.8	175.3 ± 2.3	101.4 ± 1.3
Ni	7.65 ± 0.70	8.00 ± 0.03	104.5 ± 3.9
Pb	21.6 ± 1.2	20.3 ± 1.0	94.2 ± 4.7
Zn	44.1 ± 3.3	43.6 ± 0.8	98.8 ± 1.8

Table 2

Table 2 – General information about the samples

Sample no.	Collected/ Purchased in	Product Type	Color	Brand	Country of manufacture
G1	School #1	Gouache	Blue	B1	Italy
G2	School #1	Gouache	Yellow	B1	Italy
G3	School #1	Gouache	White	B1	Italy
G4	School #2	Gouache	Yellow	B2	France
G5	School #3	Gouache	Red	B1	Italy
G6	School #3	Gouache	Yellow	B3	Italy
G7	School #4	Gouache	Orange	B4	Spain
G8	School #5	Gouache	Red	B5	Italy
G9	School #5	Gouache	Orange	B5	Italy
G10	School #6	Gouache	Purple	B5	Italy
G11	School #7	Gouache	Red	B5	Italy
G12	School #7	Gouache	Pink	B5	Italy
G13	School #7	Gouache	Green	B2	France
G14	Store #1	Gouache	Yellow	B6	Italy
G15	Store #2	Gouache	Green	B7	China
G16	Store #3	Gouache	Green	B8	France
G17	Store #3	Gouache	Magenta	B8	France
G18	Store #3	Gouache	White	B8	France
G19	Store #3	Gouache	Blue	B8	France
G20	Store #3	Gouache	Yellow	B8	France
A21	School #4	Acrylic	Blue	B1	Italy
A22	School #5	Acrylic	White	B2	France
A23	Store #1	Acrylic	Red	B9	China
A24	Store #1	Acrylic	Red (Scarlet)	B9	China
A25	Store #1	Acrylic	White	B9	China
W26	School #8	Watercolor	Golden	B2	France
W27	School #8	Watercolor	Green	B5	Italy
W28	Store #4	Watercolor	Red	B10	China
W29	Store #4	Watercolor	Orange	B10	China
W30	Store #4	Watercolor	Purple	B10	China
W31	Store #4	Watercolor	Green	B10	China
W32	Store #4	Watercolor	Blue	B10	China
W33	Store #2	Watercolor	Yellow	B11	China
W34	Store #2	Watercolor	Red	B11	China
W35	Store #2	Watercolor	White	B11	China

W36	Store #2	Watercolor	Green	B11	China
W37	Store #2	Watercolor	Yellow(lemon)	B12	China
W38	Store #2	Watercolor	Orange	B12	China
W39	Store #2	Watercolor	Blue	B12	China
W40	Store #2	Watercolor	Black	B12	China
W41	Store #2	Watercolor	Brown	B12	China
W42	Store #2	Watercolor	Blue (navy)	B12	China
W43	Store #2	Watercolor	White	B12	China
W44	Store #2	Watercolor	Yellow	B12	China
W45	Store #2	Watercolor	Purple	B12	China
W46	Store #2	Watercolor	Pink	B12	China
W47	Store #2	Watercolor	Green	B12	China
W48	Store #2	Watercolor	Red	B12	China
FP49	Store #5	Fingerpaint	Black	B1	Italy
FP50	Store #5	Fingerpaint	Green	B1	Italy
FP51	Store #5	Fingerpaint	Red	B1	Italy
FP52	Store #5	Fingerpaint	White	B1	Italy
FP53	Store #5	Fingerpaint	Yellow	B1	Italy
FP54	Store #5	Fingerpaint	Blue	B1	Italy
F55	School #2	Face paint	White	B13	France
F56	School #6	Face paint	Pink	B14	Spain
F57	School #7	Face paint	Silver	B15	China
F58	Store #6	Face paint	Pink	B16	China
F59	Store #6	Face paint	Yellow	B16	China
F60	Store #7	Face paint	White	B17	U.K
F61	Store #7	Face paint	Yellow	B17	U.K
F62	Store #7	Face paint	Blue	B17	U.K
F63	Store #7	Face paint	Purple	B17	U.K
F64	Store #7	Face paint	Green	B17	U.K
F65	Store #7	Face paint	Red	B17	U.K
F66	Store #7	Face paint	Black	B17	U.K

Table 3

Table 3 – Metals content in samples (mean value of n=3 determinations; µg g^{-1} wet weight) and summary statistics

Sample ID	Pb	Cd	Co	Cr	Ni	Mn	Cu	Zn
Gouaches (n=20)								
G1	<LoD	0.04	<LoD	0.67	0.34	35.2	400	4.22
G2	0.30	0.03	0.17	0.52	0.42	33.8	<LoD	2.81
G3	<LoD	0.04	<LoD	0.45	<LoD	5.75	<LoD	2.46
G4	0.79	0.03	<LoD	0.39	<LoD	<LoD	<LoD	3.16
G5	0.48	0.03	<LoD	1.22	0.50	46.7	<LoD	3.16
G6	<LoD	0.02	<LoD	0.16	<LoD	<LoD	<LoD	<LoD
G7	1.69	0.21	<LoD	1.07	<LoD	23.0	<LoD	3.86
G8	1.94	<LoD	<LoD	0.73	0.78	43.1	<LoD	9.84
G9	0.75	0.03	<LoD	0.49	0.51	45.3	<LoD	7.38
G10	1.14	0.04	0.32	0.52	0.78	45.3	13.1	10.2
G11	0.68	0.03	0.16	0.46	0.60	43.1	<LoD	6.32
G12	0.90	0.03	0.17	0.46	0.71	48.9	<LoD	7.38
G13	0.79	<LoD	<LoD	0.44	<LoD	5.75	361	2.81
G14	0.41	0.30	<LoD	2.39	0.27	10.8	<LoD	4.22
G15	<LoD	0.02	<LoD	0.62	0.85	<LoD	439	11.6
G16	0.39	<LoD	<LoD	0.17	0.80	<LoD	<LoD	<LoD
G17	0.51	<LoD	<LoD	0.17	0.74	<LoD	602	<LoD
G18	0.38	<LoD	<LoD	0.20	0.78	<LoD	<LoD	<LoD
G19	0.48	0.07	0.16	0.65	1.00	<LoD	<LoD	<LoD
G20	0.52	0.02	0.19	0.26	1.16	<LoD	384	<LoD
Mean (median)*	0.65 (0.50)	0.05 (0.03)	0.13 (0.10)	0.60 (0.48)	0.56 (0.56)	20.5 (8.3)	112.7 (3.9)	4.39 (3.16)
SD	0.48	0.07	0.05	0.50	0.30	19.4	197	3.26
Max.	1.94	0.30	0.32	2.39	1.16	48.9	602	11.6
Acrylics (n=5)								

A21	<LoD	0.03	<LoD	0.73	<LoD	10.8	1458	2.81
A22	0.42	<LoD	<LoD	0.10	<LoD	<LoD	<LoD	<LoD
A23	<LoD	<LoD	0.24	0.36	<LoD	<LoD	<LoD	3478
A24	<LoD	<LoD	<LoD	2.12	1.69	<LoD	<LoD	34.4
A25	0.39	<LoD	1.47	0.79	0.77	<LoD	<LoD	2968
Mean (median)*	0.29 (0.21)	0.02 (0.01)	0.40 (0.10)	0.82 (0.73)	0.60 (0.19)	4.45 (2.87)	295 (3.86)	1297 (34.4)
SD	0.11	0.01	0.60	0.78	0.66	3.54	650	1768
Max.	0.42	0.03	1.47	2.12	1.69	10.8	1458	3478
Watercolors (n=23)								
W26	0.35	<LoD	<LoD	4.88	<LoD	<LoD	7.05	9.13
W27	<LoD	<LoD	<LoD	0.21	<LoD	<LoD	12.1	327
W28	1.67	0.07	0.91	8.71	3.10	2.88	<LoD	646
W29	1.16	0.09	0.31	7.67	1.66	2.87	<LoD	538
W30	0.81	<LoD	0.22	7.40	1.39	<LoD	8.24	16.5
W31	1.71	0.12	0.53	8.01	1.34	2.88	831	204
W32	1.98	0.07	0.20	9.40	2.32	3.59	952	51.3
W33	<LoD	<LoD	<LoD	0.16	<LoD	<LoD	<LoD	<LoD
W34	<LoD	<LoD	<LoD	0.09	<LoD	<LoD	<LoD	<LoD
W35	<LoD	<LoD	<LoD	0.09	<LoD	<LoD	<LoD	13.1
W36	<LoD	<LoD	<LoD	0.16	<LoD	<LoD	441	<LoD
W37	0.30	0.03	<LoD	0.72	0.61	<LoD	<LoD	<LoD
W38	0.31	0.04	<LoD	0.76	0.63	<LoD	<LoD	<LoD
W39	0.30	0.04	<LoD	0.75	0.62	5.86	129	<LoD
W40	0.33	0.04	<LoD	0.89	0.67	4.24	<LoD	<LoD
W41	0.32	0.04	<LoD	0.76	0.63	<LoD	27.5	<LoD
W42	<LoD	0.04	<LoD	0.78	0.62	<LoD	313	<LoD
W43	0.38	0.04	<LoD	0.76	0.61	<LoD	<LoD	<LoD
W44	0.30	0.04	<LoD	0.71	0.58	<LoD	<LoD	<LoD

W45	0.30	0.04	<LoD	0.76	0.57	<LoD	<LoD	<LoD
W46	0.36	0.05	<LoD	0.84	0.72	4.62	<LoD	<LoD
W47	0.31	0.03	<LoD	0.73	0.60	<LoD	70.9	<LoD
W48	0.29	0.04	<LoD	0.73	0.58	<LoD	<LoD	<LoD
Mean (median)*	0.54 (0.31)	0.04 (0.04)	0.18 (0.10)	2.43 (0.76)	0.80 (0.61)	3.13 (2.87)	124 (3.86)	79.4 (1.40)
SD	0.54	0.03	0.19	3.28	0.73	0.75	266	180
Max.	1.98	0.12	0.91	9.40	3.10	5.86	952	646
Fingerpaints (n=6)								
FP49	<LoD	<LoD	<LoD	0.21	0.70	<LoD	<LoD	<LoD
FP50	<LoD	<LoD	<LoD	0.20	0.71	<LoD	163	<LoD
FP51	<LoD	<LoD	<LoD	0.23	0.70	<LoD	<LoD	<LoD
FP52	<LoD	0.03	0.19	0.42	1.22	<LoD	<LoD	<LoD
FP53	<LoD	<LoD	<LoD	0.19	0.71	<LoD	<LoD	<LoD
FP54	<LoD	<LoD	<LoD	0.28	0.70	<LoD	338	<LoD
Mean (median)*	<LoD	0.02 (0.01)	0.12 (0.10)	0.25 (0.22)	0.79 (0.70)	<LoD	86.0 (3.9)	<LoD
SD	-	0.01	0.04	0.09	0.21	-	139	-
Max.	-	0.03	0.19	0.42	1.22	-	338	-
Face paints (n=12)								
F55	0.71	<LoD	<LoD	0.34	<LoD	<LoD	<LoD	2.11
F56	0.55	0.08	<LoD	3.38	0.28	9.34	<LoD	3.51
F57	<LoD	<LoD	<LoD	0.35	<LoD	4.31	<LoD	<LoD
F58	<LoD	<LoD	<LoD	1.50	<LoD	20.1	<LoD	149
F59	0.32	<LoD	<LoD	0.76	<LoD	15.1	<LoD	18.3
F60	<LoD	<LoD	<LoD	0.66	<LoD	<LoD	<LoD	<LoD
F61	<LoD	<LoD	<LoD	1.24	<LoD	<LoD	<LoD	<LoD
F62	<LoD	<LoD	<LoD	1.18	<LoD	<LoD	<LoD	<LoD
F63	<LoD	<LoD	<LoD	1.28	<LoD	<LoD	<LoD	<LoD
F64	<LoD	<LoD	<LoD	0.42	<LoD	<LoD	<LoD	<LoD

F65	<LoD	<LoD	<LoD	0.73	<LoD	<LoD	<LoD	<LoD
F66	<LoD	<LoD	0.39	4.51	2.12	718	<LoD	<LoD
Mean (median)*	0.29 (0.21)	0.02 (0.01)	0.13 (0.10)	1.36 (0.97)	0.36 (0.19)	65.6 (2.9)	<LoD	15.4 (1.4)
SD	0.17	0.02	0.08	1.29	0.56	205.5	-	42.5
Max.	0.71	0.08	0.39	4.51	2.12	718	-	149

LoD (Limit of Detection) – Pb: 0.29 μg g^{-1}; Cd: 0.02 μg g^{-1}; Co: 0.15 μg g^{-1}; Cr: 0.04 μg g^{-1}; Ni: 0.26 μg g^{-1}; Mn: 4 μg g^{-1}; Cu: 5.5 μg g^{-1}; Zn: 2 μg g^{-1}.
*For median and mean calculation, results <LoD were imputed as LoD/√2 [12].

Table 4

Table 4 – Tolerable daily intake (TDI), background exposure and skin irritation/sensitization risk for the elements studied [13].

Element	TDI (μg kg^{-1} bw day^{-1})	Skin irritation and sensitization contact risk (qualitative indication)
Cd	0.5	Low
Cr(VI)	5*	High
Co	1.4	Medium
Cu	83	Low
Pb	3.6	Low
Mn	160	Unknown
Ni	10	High
Zn	500	Low

*This value only takes into account non-carcinogenic effects by Cr(VI).

Table 5

Table 5 – Summary of the relative intake indices (%)* for the different paint types

	Pb	Cd	Co	Cr	Ni	Mn	Cu	Zn
Gouaches (n=20)								
Mean	0.60	0.34	0.31	0.40	0.19	0.43	4.52	0.03
Median	0.46	0.20	0.25	0.32	0.19	0.17	0.16	0.02
SD	0.44	0.49	0.13	0.34	0.10	0.40	7.92	0.02
Max.	1.80	2.00	0.76	1.59	0.39	1.02	24.2	0.08
Acrylics (n=5)								
Mean	0.27	0.12	0.96	0.55	0.20	0.09	11.9	8.65
Median	0.19	0.10	0.25	0.49	0.06	0.06	0.16	0.23
SD	0.10	0.04	1.43	0.52	0.22	0.07	26.1	11.8
Max.	0.39	0.20	3.50	1.41	0.56	0.22	58.6	23.2
Watercolors (n=23)								
Mean	0.50	0.26	0.42	1.62	0.27	0.07	4.96	0.53
Median	0.29	0.25	0.25	0.51	0.20	0.06	0.16	0.01
SD	0.50	0.18	0.45	2.19	0.24	0.02	10.7	1.20
Max.	1.83	0.80	2.17	6.27	1.03	0.12	38.2	4.31
Fingerpaints (n=6)								
Mean	-	0.11	0.28	0.17	0.26	-	3.46	-
Median	-	0.10	0.25	0.15	0.23	-	0.16	-
SD	-	0.03	0.08	0.06	0.07	-	5.58	-
Max.	-	0.18	0.46	0.28	0.41	-	13.6	-
Face paints (n=12)								
Mean	0.14	0.07	0.16	0.48	0.06	0.72	-	0.05
Median	0.10	0.05	0.13	0.34	0.03	0.03	-	0.01

SD	0.08	0.07	0.10	0.45	0.10	2.25	-	0.15
Max.	0.35	0.28	0.49	1.58	0.37	7.85	-	0.52

* Relative intake indices (RII%) – the percentage of the *tolerable daily intake* (TDI) represented by the *estimated daily intake* (TDI), resulting from exposure to the products.

Table 6

Table 6 – Number of samples containing levels of Cr, Co and Ni above 5 µg g^{-1}, between 1 and 5 µg g^{-1} and below 1 µg g^{-1}.

	>5 µg g^{-1}			1-5 µg g^{-1}			<1 µg g^{-1}		
	Cr	Co	Ni	Cr	Co	Ni	Cr	Co	Ni
Gouaches (n=20)	0	0	0	3	0	1	17	20	19
Acrylics (n=5)	0	0	0	1	1	1	4	4	4
Watercolors (n=23)	5	0	0	1	0	5	17	23	18
Fingerpaints (n=6)	0	0	0	0	0	1	6	6	5
Face paints (n=12)	0	0	0	6	0	1	6	12	11