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Toxic elements in children's crayons and colored pencils: Bioaccessibility assessment

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Abstract: Crayons and colored pencils for children may contain toxic elements (TEs) exhibiting potential risk for children's health including cognitive development, after their ingestion, through mouthing and chewing and eventually, their accumulation. The aim of this study was to determine total content of As, Pb, Cr, Cd, Ni and Sb and estimate their bioaccessibility conducting artificial saliva extraction. Sixty samples of colored pencils and crayons from 10 manufacturers were analyzed. Microwave acid assisted digestion followed by inductively coupled plasma optical spectroscopy (ICP-OES) was performed for determination of total content of TEs. Simulation of extraction by artificial saliva was applied to get more reliable data when bioavailability is concerned. The total concentrations of TEs were higher in colored pencils than in crayons and their maximum levels were: 5.78, 9.36, 9.97, 0.615, and 6.63 mg kg^{-1} for As, Pb, Cr, Cd and Ni, respectively. Concentration of Sb was below the detection limit for all investigated samples. This study showed that concentration of As and Pb in several samples did not comply with European Union regulative. Bioaccessibility study showed the high degree of leaching of Cr and As from pencils, but regardless of extracted portions, concentrations of selected investigated TEs were below allowed levels.

Keywords: children toys; toxic elements; ICP-OES, bioaccessibility study; health risk.

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INTRODUCTION

Children are most susceptible to harmful effects of TEs, having in mind their insufficiently developed detoxication mechanisms, increased intake of food and drinks compared with adults (per unit of mass) as well as tendencies to put things from their environment, especially toys and crayons, in mouth causing the extraction of harmful substances via saliva and swallowing.[1,2] An increased exposition elevates hazardous effects with direct impact on TEs bioavailability, indirectly affecting to physiological parameters and behavioral patterns.[3,4] Drawing and painting in early childhood help children to express themselves and contribute to their physical and psychological development.[1–3] However, it must be taken into account that toys and crayons may have high levels of TEs, such as lead, arsenic, cadmium, chromium and nickel, which can provoke serious health problems.[5] Besides, there are various stabilizers, minerals and pigments, which naturally contain heavy metals and can additionally contribute to potential toxicity. For example, kaolinite, as a constituent in clay and chalk, which is used for children's crayons, contains Pb in concentration range 29–91 mg kg^{-1} of sample.[6] This is serious threat since even a multiple purification processes are frequently insufficient for their removal.

It is common knowledge that children are most vulnerable population when lead poisoning is concerned. For example, two-year old children have the highest concentration of Pb in their blood, partly because they put toys and various objects in their mouth, and recent studies showed that blood Pb concentration even less than 10 mg dm^{-3} can cause adverse health effects and/or decrease cognitive development.[7,8] Canfield *at al.*[8] have shown significant correlation between increased Pb concentration in blood and decrease of full-scale IQ in children. In order to address this problem, European Union adopted new annex[9] to the Toy Safety Directive 2009/48/EC, in late 2016 early 2017, with lower allowable limits for Pb concentrations in children's toys. For dry, brittle, powder-like and playable toys including wooden crayons this value is 2 mg kg^{-1} (instead of previous 13.5 mg kg^{-1}), and for liquid or sticker toys including water colors 0.5 mg kg^{-1} (instead of previous 3.4 mg kg^{-1}).

According to the Agency for Toxic Substances and Disease Registry (ATSDR) 2021[10] As is the first one at the Priority List of Hazardous Substances. Besides that inorganic arsenic is, according to the World Health Organisation (WHO),[11] the International Agency for Research on Cancer (IARC),[12] and the Environmental Protection Agency (EPA),[13] marked as human carcinogen. The arsenic exposure can also cause serious respiratory, gastroinestinal, hepatic, neurological, and immunological effects, as well as effects on the central nervous system and impact on cognitive development of children.[1,14,15] Different studies reported a decrease in Full Scale IQ, verbal comprehension, and working memory in children aged 6–15, associated with increased levels of As in water, urine or blood.[1,4,16] Cadmium is commonly used in Ni–Cd battery manufacturing, but it is also used as a pigment in plastic, ceramic, and glass industry.[1] Some studies reported correlation of decrease of full-score and performance IQ, with four-years children, and higher frequency of attention and behavioral disorders in children aged 7–16 years with higher levels of Cd in blood and hair.[1,4,17–21] Similarly to the Pb, EU adopted recently new limits for cadmium content in children's toys: 1.3 mg kg^{-1} (instead of previous 1.9 mg kg^{-1}) for dry, brittle, powder-like and playable toys and 0.3 mg kg^{-1} (instead of previous 0.5 mg kg^{-1}) for liquid or sticker toys.[9]

Chromium is present in our environment as a result of both natural occurring element in Earth's crust and anthropogenic activities, such as mining and industrial activities. This element is 17^{th} at the ATSDR list[10] as human carcinogenic and associated with neurological and developmental disorders.[22,23] The main source of children's exposure to cadmium, beside water and food consumption, is associated with chewing and ingestion of inedible materials.[22]

Antimony has a wide range of industrial applications including electronics, plastics and pants production.[24] This element has been used as a pigment for centuries, mainly as antimony sulphide and lead antimonite.[24] Exposure to Sb may result in eye, skin, and lung irritation, but on long-term and chronic exposure may result in the formation of antimoniosis, and causes heart, gastrointestinal, and lung diseases, including pneumoconiosis, and lung cancer.[25] According to EU legislation the permissible limits for Sb content in toys is 45 mg kg^{-1}. However, there is a significant knowledge gap in different areas (environmental chemistry, toxicology and bioavailability of antimony in the environment), and harmonization of required standards for Sb limits is needed.[24]

Human exposure to the nickel can cause various health effects, including immunologic, neurologic and reproductive disorder developments or even carcinogenic effects.[26] Beside, skin allergic reactions can occur after contact, oral intake or inhalation.[27] We are exposed to great number of nickel sources in everyday life, thus European Food Safety Authority (EFSA)[28] stated that more information should be collected based on its bioavailability in foodstuffs, all in order to facilitate the establishment of food quality standards for this metal.

Determination TEs total content is important but, having in mind that mouthing behavior plays an important role in children exposure to metal contamination in toys, pencils, and crayons, the predict of mobilization of heavy metals into saliva and their ingestion during mouthing requires additional attention. Several studies on *in vitro* bioaccessibility tests for prediction of bioavailability of metals to children are published.[4,5,29,30] Those tests were based on extraction with artificial saliva (to simulate mouthing), or/and dil. HCl (to simulate conditions in stomach).

This important topic defined our goals: to evaluate total content of As, Pb, Cr, Cd, Ni and Sb in samples of 30 coloring pencils and 30 crayons from different vendors available on the Belgrade's markets and to predict bioavailability of metals based on artificial saliva extraction.

EXPERIMENTAL

Instrumentation and operating conditions

Acid digestion of the samples was performed using microwave digestion system (CEM Mars 5, USA) equipped with polytetrafluoroethylene (PTFE) tubes.

For elements determination inductively coupled plasma optical emission spectrometer (ICP-OES) with axial view (Thermo scientific iCAP 6000 series ICP-spectrometer, USA) coupled with auto sampler Cetac ASX-510 was used. The wavelength used to determine elements were: As (189.042 nm), Cd (214.400 nm), Pb (220.353 nm), Cr (267.716 nm), Ni (231.604 nm) and Sb (206.833 nm). During the analysis, the following instrumental operation conditions were used: RF frequency 27.12 MHz; operating power, 1150 W; peristaltic pump rate: 50 rpm; plasma argon flow rate 0.5 $dm^3 min^{-1}$; argon carrier flow rate 0.5 $dm^3 min^{-1}$; sample flow rate 0.02 $cm^3 min^{-1}$.

For pH control of artificial saliva pH meter Hanna Instruments 901 was used and extraction was performed using IKA® KS 260 Basic shaker.

Materials, reagents and solutions

For the evaluation of heavy metals content, 5 packages of colored pencils and 5 packages of crayons from different manufactures / country of origin (A / China, B / Italy, C / China, D / Czech Republic, E / Germany, F / China and G / China) and different cost range were provided from Belgrade's bookstores. Six samples of different colors from each package were analyzed: three major (yellow, red, and blue) and three derived colors obtained by mixing major ones (green, orange and purple). In that way, the pool of 60 samples was created (30 samples of colored pencils, and 30 of crayons).

All solutions were prepared using analytical grade reagents and deionized water with resistivity of 18.2 MΩ cm, obtained by a Milli-Q system (Millipore, Bedford, USA). Nitric acid (65 %) suprapure quality (HNO_3, G.R., Lach-ner s.r.o., Czech Republic) and H_2O_2 30 % solution (Macron Fine Chemicals, Avantor Performance Materials, Poland) were used for sample digestion. All containers used in the experiments were previously soaked in nitric acid solution (10 %) for 24 h and rinsed with deionized water afterwards.

For ICP OES analysis, external calibration was conducted using 5 working standards obtained by dilution of multi-elementary stock solution (Titrisol, Merck, Darmstadt, Germany) containing 1000 mg dm^{-3} of As, Pb, Cd, Cr, Ni and Sb. The correlation coefficients were higher than 0.99 in all cases.

The values obtained for limits of detection (*LOD*) and quantification (*LOQ*) were calculated based on 3*SD*/*m* and 10*SD*/*m*, respectively, where *m* is the slope of the calibration curves and *SD* is standard deviation of 10 consecutive measurements of the blank, multiplied by the dilution factor used for sample preparation. For method validation, specificity, linearity, working range, accuracy, precision, *LOD* and *LOQ* were estimated and presented in Table I.

The accuracy of ICP-OES method was tested in analysis of certified reference materials (CRM), fish protein (DORM-4, National Research Council, Canada) and cooking chocolate (Standard Reference Material® 2384, National Institute of Standards & Technology, USA). The obtained recovery values were in the range 82–116 %. The precision was expressed as relative standard deviation (*RSD*) and was less than 10 % in all cases ($n = 3$, Table I).

TABLE I. Parameters of method validation for As, Cd, Pb, Cr, Ni, and Sb in ICP-OES analysis

Element	R^2	*LOD* / mg kg^{-1}	*LOQ* / mg kg^{-1}	*RSD* / %
As	0.9997	0.05	0.15	0.92
Cd	0.9996	0.01	0.03	0.94
Pb	0.9968	0.01	0.02	0.97
Cr	0.9992	0.01	0.03	0.93
Sb	0.9986	0.07	0.20	0.92
Ni	0.9998	0.07	0.20	0.94

Microwave-assisted sample preparation

The crayons and the solid pigment cores of pencils were manually crushed with a porcelain mortar and pestle to obtain smaller particles and better homogenization. Portions of 0.5 g homogenized samples were transferred to PTFE tubes and 4 cm^3 HNO_3 (65 %) and 1 cm^3 H_2O_2 (30 %) were added. The tubes were submitted to a temperature of at 200 °C for 20 min under a microwave irradiation power of 800 W. After digestion, samples were filtrated through 0.45 µm PTFE membrane filter and diluted with deionized water to the total volume of 50 cm^3. The sample preparation procedure was carried out in triplicate, including the blank solutions and certified reference materials.

Bioaccessibility study

For bioaccessibility study all pencils and crayons were subjected to leaching procedure with artificial saliva in order to simulate chemical environment in a mouth. Artificial saliva was prepared according to unified BARGE method.[31] Bioavailability tests were conducted under the controlled conditions of temperature and pH. Each sample (0.5 g) was mixed with 25 cm^3 artificial saliva and shaken for 30 min (200 rpm, 37±2 °C), filtered through 0.45 µm PTEF filter. Bioavailability tests were made in triplicate including the blank solutions.

RESULTS AND DISCUSSION

Concentration of total and oral bioaccessible toxic elements (As, Pb, Cr, Cd, Ni and Sb) in the samples of 30 colored pencils and 30 crayons from different vendors provided at Belgrade's markets were analyzed.

Prior to measurements of As, Pb, Cr, Cd, Ni and Sb concentrations, the samples were subjected to microwave acid assisted digestion. To assess the bioavailability of TEs in the samples, extraction was performed using artificial saliva, according to the procedure presented elsewhere.[31] The TEs concentrations in all aliquots were measured by ICP-OES. The obtained concentrations for the TEs, expressed as average, are presented in (Tables II and III).

Generally, the total TEs content in the majority of tested samples is higher in pencils than in crayons. Besides, the concentrations of TEs in artificial saliva extracts were much higher from colored pencils, as expected, because of the coloration of filtrate due to dissolution of solid pigment core during the extraction process. That is probably related to different material composition of crayons and pencils.

According to the recently updated European Union Directive[9], allowed concentrations of heavy metals in children's toys are as follows: As 3.8 mg kg^{-1}, Pb 2 mg kg^{-1}, Cd 1,3 mg kg^{-1}, Cr 37,5 mg kg^{-1}, Ni 75 mg kg^{-1} and Sb 45 mg kg^{-1}.

TABLE II. Concentration (mg kg^{-1}, mean value, n = 3 determinations) of As, Cd, Pb, Cr and Ni in crayons samples (C) of different manufacturers (A, B, C, D, and E) after microwave assisted acid digestion and artificial saliva extraction with summary statistics; the concentrations of Sb (total content), Cd, Ni and Sb (artificial saliva extracts) were below the method detection limits and from that reason not presented

Label	Color/ manufacturer	Method							
		Microwave assisted acid digestion					Artificial saliva extraction		
		As	Cd	Pb	Cr	Ni	As	Pb	Cr
CA1	Yellow/A	0.382	ND	0.312	0.163	ND	0.170	0.055	0.058
CA2	Red/A	0.247	ND	1.30	1.87	0.311	0.074	0.169	0.623
CA3	Blue/A	0.274	ND	0.148	0.917	ND	0.129	ND	0.362
CA4	Green/A	0.258	ND	0.949	0.889	0.241	0.084	0.165	0.286
CA5	Orange/A	0.258	ND	0.994	0.761	ND	0.099	0.154	0.264
CA6	Purple/A	0.495	ND	2.78	0.850	ND	0.141	0.167	0.208
CB1	Yellow/B	0.668	0.102	3.25	1.93	0.965	0.250	ND	0.468
CB2	Red/B	0.688	0.095	3.13	2.27	0.886	0.219	ND	0.532
CB3	Blue/B	0.783	0.118	3.44	2.37	0.997	0.298	ND	0.845
CB4	Green/B	0.962	0.122	3.07	1.54	4.20	0.305	ND	0.572
CB5	Orange/B	0.556	0.137	3.84	1.75	0.937	0.284	ND	0.403
CB6	Purple/B	0.933	0.147	6.87	1.27	4.347	0.327	ND	0.366
CC1	Yellow/C	0.402	ND	0.687	0.906	0.234	0.185	ND	0.287
CC2	Red/C	0.305	0.042	1.29	2.48	0.344	0.088	ND	0.674
CC3	Blue/C	0.390	0.032	0.032	0.974	0.253	0.149	ND	0.289
CC4	Green/C	0.397	ND	0.630	2.55	0.861	0.183	ND	0.888
CC5	Orange/C	0.386	ND	0.846	2.12	0.695	0.142	ND	0.711
CC6	Purple/C	0.276	ND	2.63	2.59	0.637	0.091	0.146	0.692
CD1	Yellow/D	0.367	ND	1.17	1.91	0.695	0.127	ND	0.484
CD2	Red/D	0.358	0.032	2.59	4.76	1.32	0.043	ND	0.596
CD3	Blue/D	0.583	ND	3.03	2.84	1.17	0.236	ND	0.750
CD4	Green/D	0.337	ND	0	2.30	0.913	0.263	ND	0.573
CD5	Orange/D	0.377	ND	0	1.33	0.613	0.164	ND	0.451
CD6	Purple/D	0.655	ND	4.94	2.17	1.17	0.315	ND	0.751
CE1	Yellow/E	0.745	ND	0	0.659	0.235	0.238	ND	0.237
CE2	Red/E	0.702	ND	0	1.20	0.975	0.302	ND	0.357
CE3	Blue/E	0.622	ND	0	1.49	3.85	0.237	ND	0.430
CE4	Green/E	0.353	ND	0	0.928	2.22	0.144	ND	0.263
CE5	Orange/E	0.392	ND	0	1.10	0.344	0.112	ND	0.269
CE6	Purple/E	0.517	ND	0	2.23	0.953	0.227	ND	0.362
Average		0.489	0.027	1.59	1.70	1.17	0.19	0.143	0.468
SD		0.202	0.049	1.76	0.906	1.18	0.082	0.044	0.208
Maximum		0.962	0.147	6.87	4.76	4.35	0.327	0.169	0.888

Arsenic content in the investigated samples was in the ranges of 1.67–5.78 and 0.246–0.9619 mg kg^{-1}, for pencils and crayons, respectively. With exception of two samples of pencils of different manufacturers (F and D), both of purple color, CPF6 (5.78 mg kg^{-1}) and CPD6 (4.15 mg kg^{-1}), arsenic concentration was below the allowable limit of 3.8 mg kg^{-1} in all others.[9]

TABLE III. Toxic elements concentrations (mean value n = 3 determinations; mg kg^{-1}) in colored pencils samples of different manufacturers (B, D, E, F, and G) after microwave assisted acid digestion and artificial saliva extraction with summary statistics; the concentrations of Sb (total content), Cd, Ni and Sb (artificial saliva extracts) were below the method detection limits and from that reason not presented

Label	Color/ manufacturer	Method							
		Microwave assisted acid digestion					Artificial saliva extraction		
		As	Cd	Pb	Cr	Ni	As	Pb	Cr
CPF1	Yellow/F	0.505	0.111	1.481	3.58	0.375	0.233	0.18	0.945
CPF2	Red/F	0.538	0.087	0.957	1.24	0.419	0.245	ND	0.259
CPF3	Blue/F	1.34	0.071	8.415	2.26	2.06	0.623	0.220	0.731
CPF4	Green/F	0.405	0.076	0.678	1.77	1.61	0.139	ND	0.637
CPF5	Orange/F	0.445	0.082	1.021	3.99	0.846	0.176	0.186	0.974
CPF6	Purple/F	5.78	0.615	8.613	1.82	3.61	2.509	0.779	0.532
CPB1	Yellow/B	0.599	0.113	1.165	1.27	0.532	0.163	ND	0.348
CPB2	Red/B	0.423	0.085	0.524	1.15	0.466	0.125	ND	0.467
CPB3	Blue/B	0.492	0.089	0.75	0.915	0.402	0.170	ND	0.246
CPB4	Green/B	0.589	0.103	0.951	0.637	0.423	0.24	ND	0.179
CPB5	Orange/B	0.442	0.107	0.942	2.62	0.532	0.184	ND	0.490
CPB6	Purple/B	1.04	0.1	0.914	5.02	0.745	0.471	0.208	0.692
CPD1	Yellow/D	0.652	0.079	1.760	4.84	2.92	0.227	ND	0.558
CPD2	Red/D	0.213	0.078	0.543	2.01	1.01	0.081	ND	0.671
CPD3	Blue/D	0.602	0.080	0.705	1.54	1.81	0.247	ND	0.597
CPD4	Green/D	0.691	0.070	2.561	2.72	2.40	0.292	0.699	0.586
CPD5	Orange/D	0.439	ND	1.517	4.59	2.48	0.168	ND	0.736
CPD6	Purple/D	4.15	0.075	4.623	1.60	0.695	1.814	ND	0.620
CPE1	Yellow/E	1.64	ND	ND	0.818	0.222	0.433	ND	0.285
CPE2	Red/E	1.14	0.127	3.311	3.85	3.28	0.413	0.525	0.793
CPE3	Blue/E	1.04	ND	ND	1.94	0.795	0.246	ND	0.257
CPE4	Green/E	1.22	0.081	1.878	0.988	0.036	0.476	ND	0.248
CPE5	Orange/E	1.12	ND	ND	1.10	0.351	0.461	ND	0.236
CPE6	Purple/E	1.68	ND	0.055	1.36	0.485	0.467	ND	0.326
CPG1	Yellow/G	0.412	0.033	0.393	11.17	6.63	0.136	0.107	1.94
CPG2	Red/G	0.286	0.039	0.185	9.44	5.62	0.097	0.042	1.99
CPG3	Blue/G	0.415	0.071	7.946	9.98	2.26	0.164	0.198	2.24
CPG4	Green/G	0.370	ND	ND	5.59	3.68	0.103	0.208	0.804
CPG5	Orange/G	0.339	ND	5.24	6.07	4.29	0.117	0.149	0.789
CPG6	Purple/G	1.06	ND	9.36	6.12	4.78	0.315	0.151	1.47
Aver.		1.002	0.079	2.22	3.40	1.86	0.385	0.281	0.722
SD		1.16	0.109	2.84	2.84	1.77	0.511	0.231	0.532
Max		5.78	0.615	9.36	11.17	6.63	2.509	0.779	2.24

Arsenic is naturally present in a yellow pigment (orpiment), as arsenic sulfide but its highest concentration was measured in purple color. In artificial saliva extracts of crayon samples, manufacturers A and C, the concentrations of As were below the detection limit, while 28.5 to 51.2 % of extracted As was found in the rest of samples. In majority of extracts obtained from pencils As was extracted up to 46.7 %. It is noteworthy that two samples with total As contents exceeded the allowed concentration (CPF6 and CPD6). In those samples the extracted portions were 43.4 and 43.7 %. These concentrations were below the allowable limit.

According to the reported data, kaolinite (contains Pb) is usually used as a component of children's crayons[8], but besides that, Pb compounds are commonly used as pigments, for example: lead (II) chromates (yellow, orange, red, and green), lead oxides (red), lead (II) carbonates (white lead) and lead molybdates (red orange).[8,32] Following the obtained results for the Pb content in crayon samples, it can be observed that the concentration of this metal varies widely among manufacturers (Tables II and III). For example, Pb concentration in all samples of crayons by manufacturer E is below the detection limits, and for all samples of crayons manufacturer B, Pb content is above the EU safety limit. Lead was detected in all colored pencils, with exception of four samples (CPE1, CPE3, CPE5 and CPG4) where it was below the detection limit. Some of the samples (manufacturers F, D, and G) had several times higher concentrations than permitted by EU regulative (CPF3 8.41 mg kg^{-1}, CPF6 8.61 mg kg^{-1}, CPD6 4.62 mg kg^{-1}, CPG3 7.95 mg kg^{-1}, CPG5 5.24 mg kg^{-1} and CPG6 9.36 mg kg^{-1}). Moreover, higher concentrations of this metal were founded in blue and purple colors. According to an earlier legislation[6], the lead content was below the allowable concentration (13.5 mg kg^{-1}) for all manufacturers. However, when updated and stricter regulations are applied, only manufacturer E met the requirement for wooden pencils and wax crayons. These results can suggest that price and, in some cases, country of origin (directives that some country follow during the manufacturing and distribution) of investigated samples are the most significant factors in potential health risk for children.

In general, lead exposure causes health problems but, more significant with children mostly because of mouthing habits, and also due to facilitated gastrointestinal lead absorption.[32] It is important to know that lead has a half-life of 35 days in erythrocytes, two years in the brain cells and decades in the bones, with evidence of greater absorption in children compared with adults.[33] According to the reported data[5] safe concentration of Pb in the blood, without effect on the children's intelligence quotient (*IQ*), is 10 mg dl^{-1}. In another study,[8] the analysis was done with 172 children aged 0.5–5 years. It was found that increase of Pb concentration from 1 to 10 mg dl^{-1}, reduces *IQ* for 7.4 units. It can be concluded that there is no safe limit for lead, so control of its content in crayons, as well as in other toys should be mandatory. The extracted portion of Pb in the artificial saliva varies up to 47 %, independently on color or the manufacturer, but none of the samples exceeded the allowable value.

Chromium concentrations were all bellow the allowable limits (0.6368–0.974 and 0.1632–4.76 mg kg^{-1} for pencils and crayons, respectively). Also, it has been observed that Cr in all samples is extracted in similar portions (20–30 %), but these concentrations are far below the permitted values. According to the literature, higher content of this metal was expected in the yellow and orange colors, because of lead (II)-chromate, which is used as a basic pigment.[5,34,35] However, the obtained results showed no correlation between Cr concentration and sample color. Guney and Zagury[36] reported that no one of 30 investigated metallic toys and jewelry exceeds the EU limit for Cr. On the other hand, Cui *et al.*[5] tested 45 children's toys and jewelry for total and bioaccessible metal concentrations and found that those items were significant source of Ni and Cr. They also emphasized the importance and need for more strict regulation of Cr concentration in toys and jewelry.

After a total digestion, Cd was detected in crayon samples of two different manufacturers: B (all colors) and C (only red and blue crayons) in the concentration range 0.032–0.147 mg kg^{-1}. In pencils, Cd was detected in range of 0.033–0.615 mg kg^{-1} in the samples of all manufacturers except the manufacturer E. It is found that concentration of Cd in all samples was below the EU limit (1.3 mg kg^{-1}) and no significant correlation was noticed between color and cadmium content. In artificial saliva extracts, concentration of cadmium was below the detection limit for all investigated samples. With exception of four wax crayons (CA1, CA3, CA5 and CA6), nickel was founded in all samples, in the range from 0.235 to 6.63 mg kg^{-1} and below the EU safety limits. Concentrations of Ni in artificial saliva extracts were all below the detection limits. Finally, concentration of Sb was below the detection limits, as well as below the EU safety limits, for all investigated samples.

CONCLUSION

The results presented in this study are important for many reasons, mostly as potential health risk for children as well as environmental issues. In general, total TEs contents, and their concentrations in artificial saliva extracts, were higher in colored pencils than in crayons, due to better dissolution of solid pigment core. Total concentrations of TEs in pencils and crayons vary widely among manufacturers, and for some samples of colored pencils concentration of As and Pb excided the levels permitted by EU legislative. Chromium and arsenic showed the very high leaching potential in bioaccessibility study (around 30 %, on average), but regardless of the portion of extracted elements by artificial saliva, all values were below the allowable limits. The differences between these two types of coloring pencils are probably related to their material composition, type of used pigments, and manufacturing process, but it was not possible to make some valid correlation without specific information and knowledge of these parameters, indicating that more research, in this field, is needed. To our best knowledge, this is the first comprehensive study, of this type, in Serbia and tends to contribute to the database of similar published reports in Europe.

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ИЗВОД

ТОКСИЧНИ ЕЛЕМЕНТИ У ВОШТАНИМ И ДРВЕНИМ БОЈИЦАМА ЗА ДЕЦУ: ПРОЦЕНА БИОДОСТУПНОСТИ

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Уобичајена навика деце да оловке жваћу или држе устима може довести до ослобађања евентуално присутних токсичних елемената и њиховог уношења у организам. Већина таквих елемената, захваљујући великом кумулативном потенцијалу, представљају потенцијални ризик по здравље деце ометајући, пре свега, њихов когнитивни развој. Циљ овог рада био је одређивање укупног садржаја As, Pb, Cr, Cd, Ni и Sb у узорцима дрвених и воштаних бојица, те процена њихове биодоступности. Испитивано је укупно 60 узорака бојица, различитих боја, 10 различитих произвођача. Узорци су припремани методом микроталасне дигестије, а за процену биодоступности примењена је екстракција вештачком саливом. Садржај испитиваних елемената је одређиван методом индуктивно спрегнуте плазме оптичке емисионе спектрометрије (ICP-OES). Укупан садржај свих испитиваних елемената је био већи у дрвеним него у воштаним бојицама и максималне измерене концентрације (mg kg^{-1}) износе: 5,78 (As); 9,36 (Pb); 9,97 (Cr); 0,615 (Cd); 6,63 (Ni). Садржај Sb је за све испитиване узорке нижи од границе детекције. Добијени резултати су показали да концентрација As и Pb у неколико узорака бојица није у сагласности са важећом регулативом Европске Уније. Испитивање биодоступности токсичних елемената је показало да су As и Cr лако екстрактабилни, али независно од процента екстракције садржај свих испитиваних елемената у екстрактима вештачке саливе је нижи од дозвољених вредности.

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