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Evaluation of Heavy Metals of Temporary Teeth From Areas with Different Pollution Level

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The aim of the paper is to evaluate the heavy metals of temporary teeth collected from areas with various environmental pollution. It is a new approach, trying to correlate the amount of heavy metals determined with inductively plasma mass spectroscopy (ICP-MS) in enamel and dentine with hydrophilic properties at interface and the type of teeth. The paper established specific correlation of the teeth type and the amount of heavy metals indicating ranges for girls and boys. Such ranges were proposed for teeth type and hydrophilic character as well.

Keywords Dentine; enamel; environmental factors; heavy metals

Introduction

Heavy metals are elements that cannot be metabolized by the body and thus are bio-accumulative. It follows that their concentration reaches toxic levels and it can be highly aggressive over time. Heavy metals are specifically aggressive for temporary teeth and stressors for oral health.

In the research field of influence of environmental factors on health, heavy metals' impact in oral health proved to be a topical approach, taking into account particularly their strong negative influence and their accumulation in time, in various structures [1,2].

In dentistry, in the last decade, the dynamic behavior of dental structures from areas with heavy metals risk became subject of some papers mainly for evaluating environmental effects on vulnerable groups of children, as their exposure and susceptibility are greater than those of adults [1–5].

The reason for selecting these topics is due to the fact that heavy metals levels in tooth layers could seem to be an important factor of long-term exposure being permanent and chronological indicators for the nutrition state and for the individual

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exposure to the metals during the children's developing period [3]. During the process of mineralization, teeth have the ability to build in their structure many metals such as cooper (Cu), magnesium (Mg), zinc (Zn), lead (Pb) and cadmium (Cd), usually the amount is in accordance with the existence of these elements in the environment. Taking into account that cooper is a bioelement which acts as an inhibitor for demineralization [4], the amount of Cu in healthy deciduous teeth seems to be greater than in teeth involved by a caries process [5]. However, despite the fact that the negative influence of heavy metals on the teeth of people is determined especially by their dosage, the exposure time and subject's individual immunity [6] are also important. Another aspect to be pointed out is the interaction between selected chemical elements as Cu [7] with toxic heavy metals as lead.

The present article is focused on the characterization of temporary teeth from areas with various heavy metals risks, and the discussed correlations between the amount of heavy metals in various types of teeth and surface properties such as microscopy and hydrophilic-hydrophobic balance.

Experimental Part

Teeth Sample Elaboration

The methodology of this study commenced with the formation of target groups composed of children from Romanian areas with various risks regarding heavy metals, taking into account all the ethics and bioethics principles. As a reference area with less pollution a small village, Patarlagele was selected and as area with high environmental risk an industrial zone around Bucharest was chosen. Despite the fact that the main cause of pollution, an old car batteries factory, is disaffected now, the heavy metals risks remain. The identification of selected regions for target group formation was based on reports of Romanian National Environmental Agency and characteristics regarding age and sex of selected children from reference and target groups were identified in the clinical reports.

Teeth Characterization

Primary teeth were collected from children of the target groups. The teeth were mechanically cut, cleaned and polished with silicon carbide slurry and investigated with a confocal microscope Leica TCS SP1, using an obiective 10X with a numerical aperture NA = 0.3. The used laser is one with He-Ne and wave length 633 nm. Surface characterization was concluded with Atomic force microscopy (AFM), performed with an APE research equipment and contact angle determination.

The surface hydrophilicity of samples was studied by measuring the static contact angle with sessile drop of distilled water deposited on the sample surface, using a Contact Angle Meter – KSV Instruments CAM 100. Wetting was evaluated by measuring the contact angle formed between the liquid drop and the solid surface.

For the heavy metals' level an ELAN DRC-e induced plasma coupled spectrometer was used (ICP-MS) and samples were taken from two different compartments: enamel and dentin. All samples (typically: 0.1–1.2 mg) were digested in 100 ml concentrated nitric acid ULTRAPURE, Fa. Merck) Acid digestion was done in a well determined volume of HNO_3 65%; after digestion, the samples were diluted 100 times and liquid fractions were analyzed. Statistical analysis with an Anova test permitted a comparison of populations.

Results and Discussions

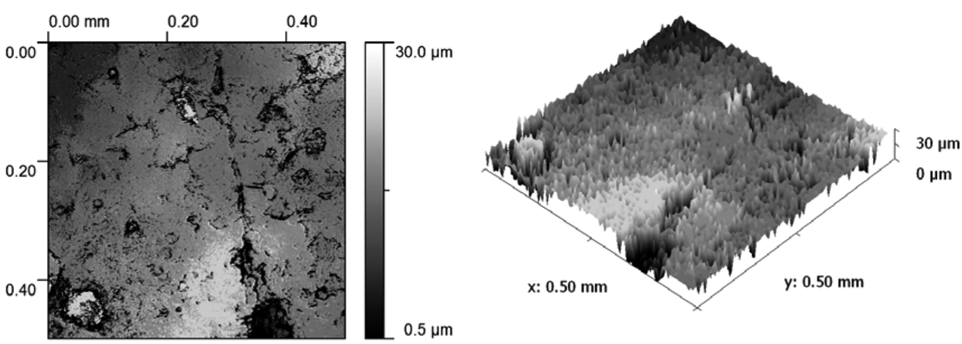
The investigation of subjects dental health was discussed in connection with teeth composition and surface aspects and according to our studies surface morphology studies. Comparison of teeth collected from reference area and from polluted area did not reveal significant differences [8,9], but at first sight teeth from Bucharest seem to be more degraded.

The topography of a sample collected from an area with environmental risk is the subject of Figure 1(a) whereas the 3D confocal image is presented in Figure 1(b). The confocal microscope image presented in Figure 1(b) reveals a degradation in depth for the same sample and this is an argument for crack in the depth of surface [9]. Figure 1 corresponds to a sample collected from a subject living in an area with high pollution and having a Cd and Pb content of 126.6 and 35.3 ppm respectively. Such correlations sustain the idea that the teeth from polluted areas exhibit holes, being in fact more degraded. Despite this fact, the subjects' examination, did not permit to conclude that temporary teeth from areas with heavy metals risks present more cavities and such sentence is subject of controversies in literature [1,10,11].

It is needed to point out that there are many factors, including nutrition and social problems which may affect the surface aspects and oral health in general and therefore a correlation is very difficult to be established. Comparing with samples from reference area, aspects of degradation as delaminating stratum seem to appear more frequently in samples around areas with environmental heavy metals risks and some connection with the elemental analysis was proposed [8]. A comparison between samples from reference area and samples around areas with environmental heavy metals risks shows that in the latter delaminating stratum seem to appear more frequently and some connection with the elemental analysis was proposed [8].

Experimental ICP/MS data obtained from primary teeth samples are presented in Tables 1–4 for both target groups with specification of type of teeth (canine, molar, etc.) and specification of children sex and age.

Data from Tables 1–4 indicated that external enamel layers tend to contain more Cd, Pb and Zn than internal layers. Despite the fact that enamel is harder and less porous than dentine, the presence of a higher amount of heavy metals in it could lay



(a) (b)

Figure 1. The topography (a) and 3D image (b) of a teeth sample collected from a high polluted area.

Table 1. Metal ions' concentration in temporary teeth Enamel – boy

Samples	Age	Type of tooth	Level of pollution risk	Mn ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Hg ppm
B2 64	12	molar	High (Bucharest)	6.1	36.3	51.7	126.6	35.3	71.1
B22 85	11	molar	High (Bucharest)	41.5	40.7	33.4	30.7	55.7	37.3
B4 65	11	molar	High (Bucharest)	53.5	54.0	51.5	37.0	51.9	46.0
B9 74	10	molar	High (Bucharest)	55.5	60.7	51.5	68.4	55.5	5.5
F4 65	10	molar	High (Bucharest)	15.5	60.6	10.0	58.8	22.4	26.7
B15 71	8	molar	High (Bucharest)	22.2	40.7	33.5	99.0	51.5	33.7
B6 84	6	molar	High (Bucharest)	36.6	56.8	51.5	35.8	26.2	11.2
M22 51	12	incisor	Reference (Patarlagele)	12.2	35.9	16.7	35.9	6.6	7.0
M17 65	11	incisor	Reference (Patarlagele)	22.3	68.2	32.6	21.0	7.8	9.2
B7 8.2	8	incisor	High (Bucharest)	40.6	42.0	40.8	43.3	40.9	19.4
F 10 51	12	canine	High (Bucharest)	3.5	4.5	1.3	15.3	5.5	15.5
M20 63	11	canine	Reference (Patarlagele)	1.4	0.6	1.0	5.8	1.2	19.9
M 15 55	10	canine	Reference (Patarlagele)	22.1	60.4	12.2	61.7	0.6	7.8
F8 74	8	canine	Reference (Patarlagele)	62.2	62.4	66.0	61.4	61.8	9.8

in the atoms' (or ions) dimensions or the sorption properties of capillars in porous material.

Regarding the Ca amount, it is necessary to point out that like in bones, calcium can be partially substituted by a small amount of heavy metals as lead and cadmium and such demineralization is well known and may also take place in a tooth structure. The demineralization process can be estimated from the decrease in the ratio Ca/P in teeth. The atomic ratio (%) between Ca and P was calculated in all studied cases for both enamel and dentine and remained pretty close to the normal ratio in bone.

A statistical treatment of Tables 1–4 data concludes that the average concentration of Cu and Cd was statistically lower for girls from reference area in comparison to the concentration of deciduous teeth for girls from areas with heavy metals risks. The statistical program indicated a similar observation for boys in the case of Cu and Pb. The correlations between the teeth type and the amount of heavy

Table 2. Metal ions' concentration in temporary teeth Enamel – girl

Samples	Age	Type of tooth	Level of pollution risk	Mn ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Hg ppm
B24 55	11	molar	High (Bucharest)	44.6	40.3	39.7	37.2	27.4	23.1
B21 63	10	molar	High (Bucharest)	64.4	54.1	62.7	46.3	58.4	33.3
6.2 B8	7	incisor	High (Bucharest)	26.6	59.9	34.3	42.9	36.6	26.2
F2 75	7	incisor	High (Bucharest)	22.2	72.4	66.8	13.3	15.9	28.9
6.3 B3	8	canine	High (Bucharest)	54.7	54.1	51.8	51.0	54.5	29.3
M11 63	6	canine	Reference (Patarlagele)	12.1	53.4	7.3	49.8	0.2	4.2
5.1 M1	8	molar	Reference (Patarlagele)	10	52.6	4.6	43.2	10.2	14.5

Table 3. Metal ions' concentration in temporary teeth Dentine – boy

Samples	Age	Type of tooth	Level of pollution risk	Mn ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Hg ppm
B2 64	12	molar	High (Bucharest)	4.9	27.8	45.7	99.8	12.3	32.8
B22 85	11	molar	High (Bucharest)	39.2	39.5	25.4	19.5	24.5	22.1
B4 65	11	molar	High (Bucharest)	45.5	44.5	43.2	25.9	35.6	19.6
B9 74	10	molar	High (Bucharest)	36.2	54.8	42.0	58.9	27.8	0.8
F4 65	10	molar	High (Bucharest)	10.0	52.6	4.6	43.2	10.2	14.5
B15 71	8	molar	High (Bucharest)	14.8	31.2	24.8	82.7	19.8	14.2
B6 84	6	molar	High (Bucharest)	25.7	44.9	45.3	26.9	14.5	0.9
M22 51	12	incisor	Reference (Patarlagele)	9.8	25.6	7.2	24.3	4.2	4.2
M17 65	11	incisor	Reference (Patarlagele)	18.0	59.7	25.3	10.9	3.3	3.2
B7 8.2	8	incisor	High (Bucharest)	32.9	37.0	29.8	31.4	16.7	11.8
F 10 51	12	canine	High (Bucharest)	1.2	2.5	0.9	7.2	3.6	7.8
M20 63	11	canine	Reference (Patarlagele)	0.4	0.2	0.4	3.4	0.7	10.0
M 15 55	10	canine	Reference (Patarlagele)	12.1	53.4	7.3	49.8	0.2	4.2
F8 74	8	canine	High (Bucharest)	54.2	54.8	53.9	48.7	32.0	3.6

metals (only for samples from polluted areas) indicated various ranges both for girls and boys in enamel and dentine, as examples:

For Pb enamel: boys ≥ molar ≥ incisor ≥ canine; girls ≥ canine ≥ molar ≥ incisor;

For Cd enamel: boys ≥ molar ≥ incisor ≥ canine; girls ≥ canine ≥ molar ≥ incisor; For Pb dentine: boys ≥ molar ≥ canine ≥ incisor; girls ≥ canine ≥ molar ≥ incisor;

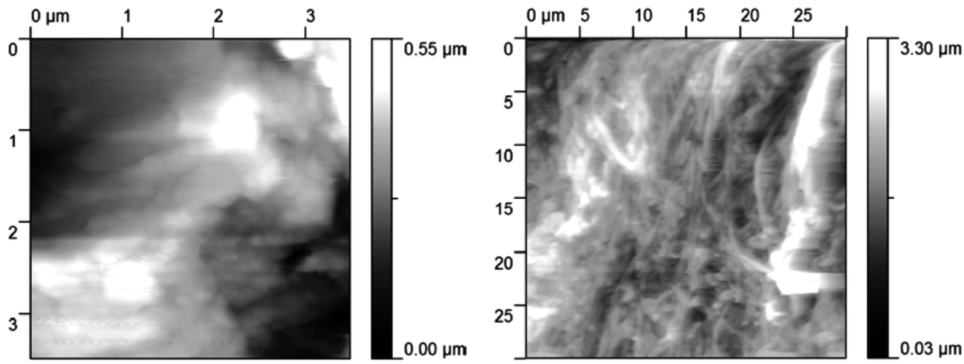
For Cd dentine: boys ≥ molar ≥ incisor ≥ canine; girls ≥ canine ≥ molar ≥ incisor;

The surface is affected especially at the enamel level, despite the fact that the amount of heavy metals released from teeth is greater in the case of dentine.

In Figure 2 are AFM images of teeth from areas with high pollution and from reference area and the figures reveal that teeth present surfaces with important average roughness as 8.8 nm and 4.3 nm respectively.

Table 4. Metal ions' concentration in temporary teeth Dentine – Girl

Samples	Age	Type of tooth	Level of pollution risk	Mn ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm	Hg ppm
B24 55	11	molar	High (Bucharest)	37.8	32.1	32.1	31.2	18.6	21.4
B21 63	10	molar	High (Bucharest)	51.4	46.3	51.9	33.4	22.5	15.6
6.2 B8	7	incisor	High (Bucharest)	20.8	46.2	22.3	37.0	14.3	24.3
F2 75	7	incisor	High (Bucharest)	20.6	61.4	55.6	0.9	0.9	13.2
6.3 B3	8	canine	High (Bucharest)	47.6	43.2	47.2	38.7	26.9	11.5
M11 63	6	canine	Reference (Patarlagele)	10.3	45.4	6.3	40.5	0.2	3.9
5.1 M1	8	molar	Reference (Patarlagele)	9.1	44.7	4.1	37.8	9.7	12.6



(a) (b)

Figure 2. AFM images of tooth selected from teeth from (a) areas with high pollution and (b) from reference area.

The analysis of 2D images for studied samples using the program Image J indicated an average porosity with a 0.08% value, and the maximum and minimum porosity being 0.11% and 0.05% respectively. The samples with maximum and minimum porosity have also the minimum and maximum amount of Hg. The Image J program permitted an evaluation of pores diameters and all values were situated in 0.018 mm–0.025 mm interval, the arithmetic average being 0.022 mm and the average number of pores/mm^2 having 8.1 value.

The porosity and roughness were explored in connection with surface wettability, which is identified as a key property of solid surfaces such as teeth [12]. Young [13] considered the equilibrium state between forces acting on the contact line separating wetted and unwetted portions of a homogenous smooth solid surface and showed that the contact angle between liquid droplet and surface depends on interfacial properties. As interfacial properties the energy surface–liquid, surface vapor and vapor liquid were taken into consideration.

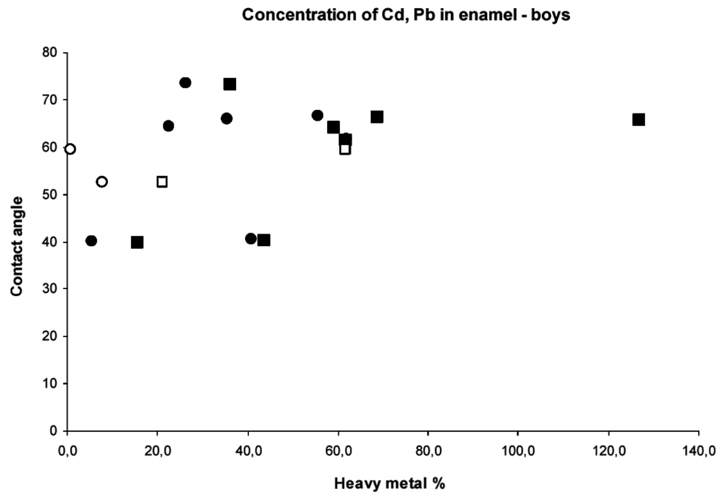
Having data from previous work regarding cell viability on temporary teeth [2] from high polluted areas and their content in heavy metals [8], and knowing that the hydrophilic-hydrophobic balance is a critical factor influencing adhesion of biological cell, Figures 3 and 4 tried to connect wettabiliy with teeth and interface type, dentine or enamel respectively. As it can be seen from Figures 3 and 4, all contact angle data are in the hydrophilic domain; however, the teeth collected from high pollution risks areas resulted in samples with less hydrophilic character in comparison with the reference area, thus being in agreement with previous results [11,13]. As it is expected, a clear correlation can be made between the heavy metals content (Pb, Cd) and wettability of teeth's dentine, their surfaces being smoother in the case of teeth from lower polluted areas.

A statistical treatment of data introduced in Figures 3 and 4 concludes that dentine is more hydrophilic compared with enamel samples, for each sample of deciduous teeth.

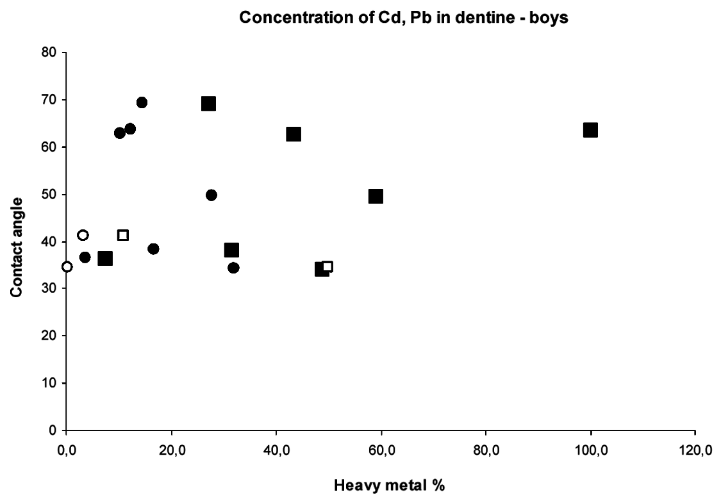
The correlation of the teeth type and hydrophilicity indicated the following ranges both for girls and boys:

For enamel: boys $\geq$ molar $\geq$ canine $\geq$ incisor; girls $\geq$ molar $\geq$ canine $\geq$ incisor;

For dentine: boys $\geq$ molar $\geq$ canine $\geq$ incisor; girls $\geq$ molar $\geq$ canine $\geq$ incisor;



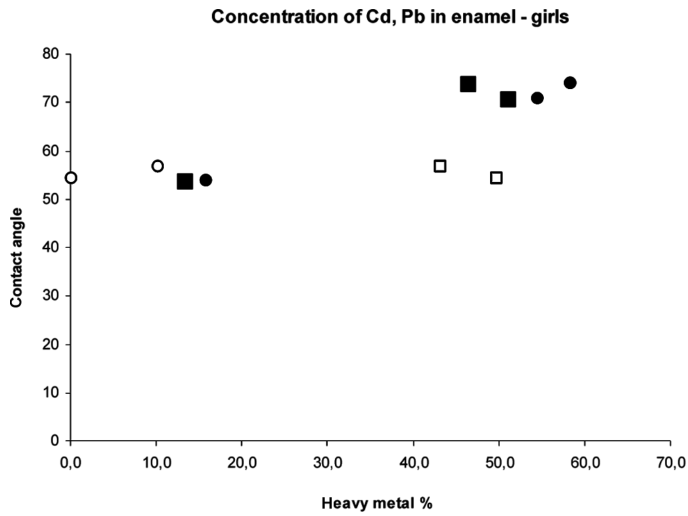
(a)



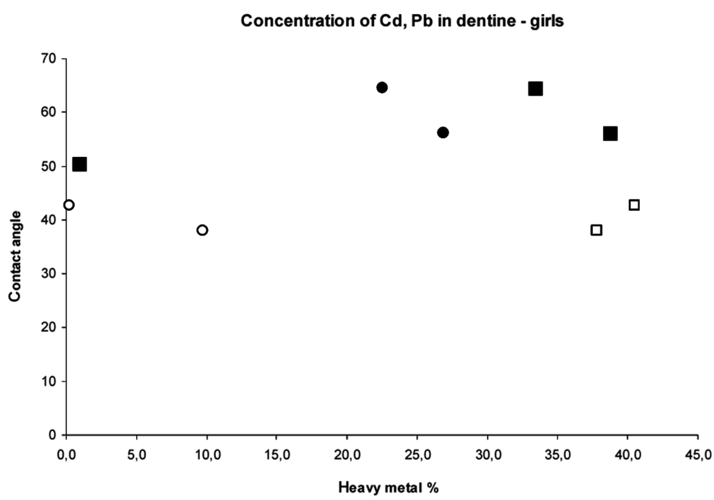
(b)

Figure 3. (a) Contact angle values for enamel – boys: ■ – Cd, ● – Pb, □ – reference Cd, ○ – reference Pb; (b) Contact angle values for dentine – boys: ■ – Cd, ● – Pb, □ – reference Cd, ○ – reference Pb.

For both boys and girls, approximately the same behavior can be observed from a hydrophilic/hydrophobic balance point of view. It is well known from literature that the wetting of a surface by liquid is affected by the surface's roughness [14]. On very rough surfaces, contact angles are larger than on chemically smooth surfaces [15]. The effect of surface roughness on the hydrophobic-hydrophilic balance in the model developed by Wenzel [16] is explained by the idea that both hydrophobicity and hydrophylicity are reinforced. According to this model, the hydrophilic surface becomes more hydrophilic and the hydrophobic one becomes more hydrophobic as a result of a process where the liquid fills the existing space on the surface as protrusions.



(a)



(b)

Figure 4. (a) Contact angle values for enamel – girls: ■ – Cd, ● – Pb, □ – reference Cd, ○ – reference Pb; (b) Contact angle values for dentine – girls: ■ – Cd, ● – Pb, □ – reference Cd, ○ – reference Pb.

It should be emphasized that the surface engineering properties of solid materials as teeth established the importance of wetting phenomena which occur in micro and nanoscale, because molecules located along the three phase contact line may have a different energy and high resolution wettability modification is studied today under controlled temperature and pressure conditions using ultra performance procedures [12,17,18]. It provides assistance to understanding and monitoring oral health.

Conclusions

1. The average concentration of Cu and Cd determined with ICP-MS method, were statistically lower for deciduous teeth of girls from reference area in comparison to the concentration of deciduous teeth of girls from area with heavy metals risks.
2. The average concentration of Cu and Pb of temporary teeth of boys from reference area and areas with high risk of heavy metals were statistically higher in comparison to the concentration of deciduous teeth of girls from the same area.
3. A range dependence of the heavy metals' concentration in teeth type was established as well as a relation between teeth type and the hydrophilic/hydrophobic balance.
4. A comparison between samples from reference area and samples around areas with environmental heavy metals risks shows that in the latter aspects of degradation as delaminating stratum seem to appear more frequently.

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