Distribution and interactions of priority heavy metals with some antioxidant micronutrients in inhabitants of a lead-zinc mining community of Ebonyi State, Nigeria

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Abstract

Background: Human exposure to xenobiotics, especially priority heavy metals (lead, cadmium, arsenic, mercury and chromium), is unavoidable because of their involvement in industrial applications, accumulation in the environment over time and non-biodegradability. Unfortunately, they induce unprecedented biochemical and pathological changes on those exposed to them, causing oxidative damages and organ toxicities.

Aim: This study investigated the frequencies of priority heavy metals and their impact on some micronutrient elements (copper, iron, zinc) in the blood of inhabitants of a lead-zinc mining community in southeastern Nigeria.
Introduction

Heavy metals are naturally-occurring metallic elements with high atomic weight and density at least five times greater than that of water [1]. Some of these elements such as cobalt (Co), copper (Cu), iron (Fe), Nickel (Ni), selenium (Se), and zinc (Zn) are actually necessary for humans in minute amounts while others such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb) and mercury (Hg) can damage living things even at low concentrations and tend to accumulate in the food chain [2]. The elements in the first group are the essential micronutrients – they are absolutely needed by the body even though in minute amounts. These micronutrients are known to play great roles in cellular metabolism including fetal growth and survival, anti-oxidization and cellular maintenance [3,4]. Particularly, zinc, copper and selenium are antioxidants known to be involved in reproduction. Zinc and copper increase sperm count and motility, and help to extend the functional life span of ejaculated spermatozoa [5] while selenium is an essential structural protein in spermatozoa [6]. Iron and copper are involved in hemoglobin synthesis while zinc and selenium are involved in immune development and maintenance, hence sometimes referred to as anti-infective antioxidants [7]. Those in the second group are the toxic elements that have been implicated in toxicity of many organs, especially the liver and the kidney [8–10]. Because of their high degree of toxicity and persistence in the environment, As, Cd, Cr, Pb and Hg are commonly considered as priority heavy metals that are of public health importance [1,11]. They are highly hazardous and can negatively affect our health and environments when improperly managed, hence regarded as serious environmental pollutants. Four of these priority heavy metals (As, Cd, Pb, Hg) are among the ten major chemicals of concern [12]. Sources of these heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents and the atmosphere [13].

Environmental pollution is very prominent in point source areas such as mining, foundries, smelters, and other metal-based industrial operations. In Enyigba community in Ebonyi State of Nigeria, environmental contamination and human exposure to heavy metals result from artisanal lead–zinc mining activities which have become a significant occupation among most of the inhabitants, both old and young. With such artisanal mining activities and the inappropriate storage of the mined products in their homes and heaps of the mining tails everywhere in the community [14], the inhabitants (both miners and non-miners) are bound to be exposed to metal pollution. Earlier assessment of herbal preparations from the study area [15], suggests that there is possibility of heavy metal intoxication of the inhabitants in addition to attenuation of the phyto–potency of the preparations by the heavy metals. This is supported by earlier findings on the concentrations of these heavy metals in the soil, water and foods from this area and its environs [16–18].

Some studies [19–21], have evaluated the interactions between toxic elements and nutritional essential elements generally, while some [22–24], were particularly on lead-exposed workers. Apart from these earlier studies, there is dearth of data on the frequencies and interactions between priority heavy metals and nutritional elements in point source area like a mining community, comparing miners and non-miners living in the same community. In the present study, we investigated for the first time, all five priority heavy metals in the blood of occupationally-exposed and environmentally-exposed subjects in a lead–zinc mining community, and their interactions with some essential micronutrient elements. Elucidating such interactions is essential for health risk assessment and management of chemical mixtures. Also, understanding the interactions in both occupationally and environmentally-exposed individuals will help government of the day to enact legislations enforcing proper disposal mechanisms for the products of both artisanal and formal mining activities and possibly plan effective phyto–remediation of the mining areas. These will go a long way in safeguarding the lives of the inhabitants of these mining communities.

Materials and methods

Ethical considerations

Ethical clearance for this study was sought and obtained from the Health Research Ethics Committee of the College of Medicine, University of Nigeria Teaching Hospital, Ituku-Ozalla, Enugu, Nigeria. Further ethical clearance was obtained from the State Ministry of Health, Abakaliki, Ebonyi State, Nigeria. The subjects gave their informed consent after thorough explanation of the importance and procedures for the study.

Study area

Enyigba mining community is the largest and most active among mining sites in Abakaliki mining area. The Abakaliki mining area lies between latitude 6°08’ N and 6°24’ and longitudes 8°05’S, with a prevailing climate condition of high...
temperatures and humidity for more than half the year and mangrove and freshwater swamp vegetation. The inhabitants are mainly subsistent farmers with yam and plantain as their staple foods, with oil palm bush and indigenous trees of nutritional, economic, medicinal and cultural importance. The Abakaliki lead–zinc is believed to be of hydrothermal origins emplaced at a temperature of about 140°C [17]. The region includes Abakaliki town (the state capital of Ebonyi State in the south eastern part of Nigeria) and the highly mineralized rural community (Enyigba) which is about 14 km south of the metropolis. Ezzamgbo, which is about 25 km from the study area, with no history of mining activities was used as a control community.

Subjects

A total of 215 subjects (aged between 10 and 60 years) were recruited for the study, comprising 89 artisanal mine workers (occupation-exposed), 61 non-mine workers but living in the community (environmentally-exposed) and 65 subjects who lived 25 km away from the mining community who were not involved in any mining activity (controls).

Sample collection and analysis

Four milliliters (4.0ml) of venous blood was collected from each subject into sequestrene containers for heavy metal analysis. The separated plasma samples were stored frozen at -80°C till day of analysis. The heavy metals comprising priority heavy metals (Arsenic, Cadmium, Chromium, Lead, Mercury) and essential elements (Copper, Iron, Zinc) were estimated by flame atomic absorption spectrometry using FS240AA Atomic Absorption Spectrophotometer (Agilent Technologies, USA) according to the method of American Public Health Association [25].

Data analyses

Data were analyzed using the statistical package for social sciences (SPSS). Statistical significance was taken to be p<0.05 in all the analyses.

Results

Table 1 represents the frequencies of the priority heavy metals in the study participants in comparison with the WHO recommended limits. Pb was the most frequent with 148 out of 150 participants (98.66%) with limits of 10 μg/dl and above. This was followed by Cd (56.66%) and As (54.00%) based on their respective recommended limits.

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Recommended limit</th>
<th>Occup. Exposed Mean (SD)</th>
<th>Environ. Exposed Mean (SD)</th>
<th>Control Mean (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (μg/dl)</td>
<td>&lt;10 μg/dl</td>
<td>148 (98.66)</td>
<td>85 (56.66)</td>
<td>85 (56.66)</td>
</tr>
<tr>
<td>Cd (μg/l)</td>
<td>0 – 5 μg/l</td>
<td>85 (56.66)</td>
<td>85 (56.66)</td>
<td>85 (56.66)</td>
</tr>
<tr>
<td>As (ng/ml)</td>
<td>0 – 12 ng/ml</td>
<td>81 (54.00)</td>
<td>81 (54.00)</td>
<td>81 (54.00)</td>
</tr>
<tr>
<td>Hg (μg/l)</td>
<td>&lt;10 μg/l</td>
<td>70 (46.66)</td>
<td>70 (46.66)</td>
<td>70 (46.66)</td>
</tr>
</tbody>
</table>

The Spearman correlations between blood priority heavy metals of the study population are presented in Table 4. There were significant positive correlations between blood Pb and each of Hg (r = 0.327, p<0.000), As (r = 0.537, p<0.000), Cd (r = 0.352, p=0.000) and Cr (r = 0.183, p=0.009). There were also significant correlations between Cd and Hg (r=0.402,
p=0.000), and between As and each of Hg (r=0.213, p=0.002) and Cr (r=0.159, p=0.024).

Table 5 presents correlations between the blood priority heavy metals and some essential trace elements in the study population. There were significant negative correlations between blood levels of the priority heavy metals and the trace elements (Zn, Fe, Cu), except between Hg and Cu (r = -0.046, p = 0.518); and between Cr and Cu (r = -0.137, p = 0.053).

**Discussion**

Although lead and other WHO priority heavy metals (mercury, arsenic, cadmium and chromium) induce physiological, biochemical and behavioral disturbances of much pathological magnitude in humans, exposure to these xenobiotics is unavoidable because of its accumulation in the environment and use in industrial application [26]. Being present in contaminated water, air, soil, food and dust, heavy metals are mostly absorbed by the lungs and gastrointestinal tract [27]. The results of this study revealed that the frequencies of the priority heavy metals – lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr) and arsenic (As) in occupationally-exposed subjects were above their recommended limits and also significantly higher when compared with environmentally-exposed and control subjects. These findings are in agreement with some earlier studies on blood heavy metal concentrations in human subjects in similar environments [21,24,28]. However, Ji, et al. [29] reported lower blood lead levels and other heavy metals amongst children. This difference may be attributed to length of exposure of these subjects to the metals' sources. This opinion sounds plausible because heavy metals are known to be non-biodegradable with long biological half-life, making them to accumulate over time [30]. Furthermore, the study also indicates that environmentally-exposed subjects are at risk of heavy metal toxicity and micronutrient deficiency given the significant differences between the values of these metals in this group and those in the control group. In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondria, lysosome, endoplasmic reticulum, nuclei and some enzymes involved in metabolism, detoxification and damage repair – antioxidant mechanism, carcinogenesis or apoptosis [31]. These metal ions were found to interact with cell components such as DNA and nuclear proteins, causing alterations in cell activities [31].

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It is needed for the functioning of these enzymes, playing vital component of more than 300 different metalloenzymes where metalloenzymes, most of which help to inactivate free radicals of red blood cells, copper is an integral component of many maintenance of life and health and also act as antioxidants that exert numerous biochemical and physiological functions for the body by encouraging oxidative stress, but also competes with lead for similar binding sites [21]. Competitive binding to metallothioneine-like transport protein in the rat duodenum demonstrates the ability of zinc to reduce lead absorption and toxicity. Thus, zinc supplementation was found to reverse the inhibition of the activity of blood 6-amino levulinic acid dehydratase (ALAD) by lead, as it competes for and effectively reduces the availability of binding sites for lead uptake [21,24]. Furthermore, in vitro studies had indicated that lead not only impairs iron binding to transferrin, but also suppresses its synthesis thus decreasing mRNA and protein levels [50]. Also, Klauder and Petering [51] had earlier observed that many characteristics of anemia due to lead are similar to those of copper deficiency and postulated that lead may induce copper deficiency and this will interfere with iron metabolism and utilization. Copper is known to have a role in the absorption of iron because the oxidation of ferrous iron to ferric state in haem synthesis is done by ceruloplasmin. On the other hand, high levels of blood lead was found to reduce the copper ceruloplasmin levels in rats while a decreased dietary copper level was associated with increased erythrocytes lead concentration [52]. Therefore, the depletion of copper in this study may cause impaired iron absorption and contribute to the iron deficiency. In plants, heavy metals are known to alter nutrient uptake processes and antioxidant systems of forage grasses including alterations in the amino acid metabolism, photosynthetic system, syntheses of chlorophyll and carotenoids and in the cell structure [53,54]. Thus, it is suspected that forage grasses whose contents of Cu and Zn are reduced when cultivated in the presence of toxic elements like Cd and Pb may have limited growth and therefore inefficient if used in phyto-remediation of environments with high heavy metals concentrations [55].

Interaction between other priority heavy metals (Hg, As, Cd and Cr) and major trace elements (Zn, Fe and Cu) was also found in humans, and in the milk of nursing mothers [36]. The study [36], reported significant negative correlations between some priority heavy metals (Hg, As, Cd, Cr) and the trace elements (Zn, Fe, Cu) respectively which was in agreement with the present study and some previous studies [37,56].
measures are not put in place to safeguard the lives of the subjects. It is therefore expected that if adequate precautionary
significances from the two groups were
subjects are prone to the adverse effects of these priority
occupationally-exposed and environmentally-exposed
elements. Unfortunately, the results also indicate that both
activities and other biological functions of the micronutrient
metabolism of the micronutrients and therefore the antioxidant
heavy metals and the antioxidant micronutrients, indicating
results also showed negative correlations between the priority
heavy metals, apart from lead, are also prevalent in the studied area
higher in females of occupationally-exposed than males,
while this area needs further study for full elucidation and articulation to adduce any
biochemical or physiological reasons for these differences, it is
possible that the differences may have to do with the levels of
antioxidant elements in the different study groups.

Conclusion

The results of this study indicate that other priority heavy metals,
apart from lead, are also prevalent in the studied area
and in higher frequencies than WHO recommendations. The
results also showed negative correlations between the priority
heavy metals and the antioxidant micronutrients, indicating
that these priority heavy metals can affect the absorption
and metabolism of the micronutrients and therefore the antioxidant
activities and other biological functions of the micronutrient
elements. Unfortunately, the results also indicate that both
occupationally-exposed and environmentally-exposed
subjects are prone to the adverse effects of these priority
heavy metals because the values of both priority heavy metals
and antioxidant micronutrients from the two groups were
significantly different from the values obtained from control
subjects. It is therefore expected that if adequate precautionary
measures are not put in place to safeguard the lives of the
inhabitants of this area, their health status will be jeopardized.

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