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Occupational and environmental lead exposure to adolescent workers in battery recycling workshops

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Abstract

Lead (Pb), as other environmental neurotoxicant substances, has the capability to interfere with many biochemical events present in cells throughout the body. In the present study, the environmental and occupational exposure to Pb has been assessed by analyzing the scalp hair samples of male adolescents aged 12–15 years, who have worked for the last 12–36 months in Pb battery recycling workshops (BRWs). For comparative purposes, gender and age-matched subjects living in the vicinity of recycling workshops as well as in areas without industrial activity were used as controls. The scalp hair samples were oxidized by acid in a microwave oven prior to determination of Pb by electrothermal atomic absorption spectrometry. The results indicated that both workers and nonworking exposed subjects had higher levels of Pb than nonexposed controls. The contents of Pb in scalp hair of adolescent workers in the present study were compared with those reported in other studies.

Keywords

Lead, scalp hair, exposed boys, worker boys, adolescent, battery recycling workshop

Introduction

Lead (Pb) is an element that has no known physiological function in humans but adversely affects a variety of fundamental biochemical processes (Pokras and Kneeland, 2008). Many reports have shown that Pb exposure continues to be a major public health problem worldwide (Hazard, 2002; Lidsky and Schneider, 2003; Zhi et al., 2000). Pb is a neurotoxicant present in cells throughout the body and can produce a wide spectrum of alterations in many organs and has the capability to interfere with many biochemical events, especially in children and adolescents, (Jarosinska et al., 2004; Mansouri and Cauli, 2009).

Pb exposures in the workplace are responsible for a wide range of health impacts (Basaran and Undeger, 2000; Bener et al., 2001; Danadevi et al., 2003; Hsiao et al., 2001). Nowadays, in developing and developed countries, the practice increases to consume Pb, which is obtained from recycling activities (Franco-Netto et al., 2003), whereas the main consumption of Pb in whole world is in the manufacture of Pb–acid batteries (Gottesfeld and Pokhrel, 2011). The assessment of human exposure to toxic metals in the environment through measurement of those chemicals or their metabolites in human specimens is termed biomonitoring (Angerer et al., 2007; Parsons and Barbosa, 2007).

Most clinical methods used to diagnose trace element deficiencies or to assess environmental or occupational exposure to toxic elements rely on the analysis of blood, serum/plasma, and/or urine specimens. However, the choice of appropriate specimen depends on several factors, such as toxicokinetics (time of appearance and residence time of the biological parameter), the convenience or invasiveness of the specimen collection procedure, and the potential for its contamination. Thus, the appropriate selection and measurement of biomarkers is of critical importance for health care management purposes, public health decision making, and

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primary prevention activities. Several alternative, that is, nontraditional, specimen matrices including saliva, hair, and nails (Pereira et al., 2004; Slotnick and Nriagu, 2006; Wilhelm et al., 2002), that permit noninvasive collection procedures have been explored. Trace element analysis in hair samples has been widely used to assess human exposure to different contaminants present in the environment (Pereira et al., 2004). Several advantages were mentioned for the use of this specimen, that is, noninvasively collected, easily stored, and transported to the laboratory for analysis (Wenning, 2000).

In opposition, some limitations were described for hair analysis, mainly the occurrence of exogenous contamination that contributes to a differential increase in the total contents of different contaminants (Frisch and Schwartz, 2002, Rodrigues et al., 2008). In spite of these constraints, scalp hair has been considered a good screening tool to assess the likely occurrence of environmental exposures and to justify the widespread studies, that hair tissue is an accumulator for trace metals, and can be a better dosimeter than blood for tracing most of the heavy metals (Zaida et al., 2007). Hair analysis has become important to estimate the degree of human exposure to some toxic elements (Sera et al., 2002).

Over the past several years, Pb poisoning has attracted growing attention in the developed countries. At the same time, however, this problem has not been a subject of concern in most developing countries including Pakistan, with low literacy rate. Less work has been done on environmental Pb exposures and its impact on growing children in Pakistan. Due to poverty and lack of educational facilities, parents send their boys (aged 10–15 years) for different labors, including dish washing, packing different materials, and automobile workshops. In developing countries, escalation in the transportation sector is creating a growing demand for Pb–acid batteries and presumably, the recycling of used batteries.

The recycling of Pb–acid batteries is one of the greatest potential source of risk, especially for exposed workers in the informal sectors. In many developing countries, retired batteries are still broken manually using an axe, which is extremely dangerous to the workers. Inhaling dust, fumes, or vapors dispersed in the workplace air can lead to acute Pb poisoning. In Pakistan, small workshops, which has created occupational exposures or hazards, are moved or transferred from industrial zone to thickly populated domestic areas, where regulatory enforcement are less stringent. The owners recruited boys instead of men as workers on less salary. They do not obey the rules set by International Labor Organization for the child labor standards on the minimum age for starting work and the Worst Forms of Child Labor (ILO, 1973, 1999).

The small battery recycling workshops (BRWs) are scattered all over the big cities of Pakistan and they process domestically generated battery scrap. They have not any modern tool and reservoirs for acid of batteries. The workers of BRW recovered the Pb by separating the different materials (plastic material and acid) of the batteries. While the Pb cells are broken into small pieces and heated to remove combustable material, the separated materials are further sold to other industries.

In the present study, we aimed to evaluate the Pb exposure to adolescent (boys) laboring in BRWs. The study population of boys was categorized in to three groups, worker boys (WBs), those working in BRW; exposed boys (EBs), resided in the vicinity of BRW; and referent boys (RBs), residents of urban domestic areas devoid of any industrial activities. The resulted data of the present study was compared with literature reported study on exposed and nonexposed children of different age groups.

Materials and methods

Chemicals and reagents

Ultrapure water obtained from ELGA labwater system (Bucks, UK), was used throughout the work. All chemicals and reagents were of high analytical grade. For the accuracy of methodology, the certified reference material (CRM) of human hair BCR 397 (Brussels, Belgium) was used.

Instrumentation

The analysis of Pb was carried out by means of a double beam Perkin–Elmer atomic absorption spectrometer model A Analyst 700 (Norwalk, Connecticut, USA) equipped with a graphite furnace HGA-400, pyro-coated graphite tube with integrated platform, an autosampler AS-800, and deuterium lamp as background correction system. Single element hollow cathode lamp of Pb (Perkin Elmer) was used. Portions of both standard/sample and modifier were transferred into auto-sampler cups and 20 μL (standard or sample volume of 10 μL + 10 μL of modifier in each case) was injected. Argon gas (200 mL/min) was used as the purge gas except during the atomization step. The graphite furnace heating program was set

Table 1. Clinical and biochemical characteristics of referents, exposed, and worker boys.

Parameters	Referent boys	Exposed boys	Worker boys	Normal range
Serum ferritin (μg/L)	33.6 ± 3.51	28.7 ± 2.35	26.7 ± 1.58	>30
Hemoglobin (g/dL)	12.5 ± 0.53	11.8 ± 1.49	10.7 ± 0.38	11.5–16.5
Haematocrit (%)	46.5 ± 3.2	40.3 ± 2.84	35.2 ± 2.56	35–55
Red blood cell count (M/ mm^3)	4.5 ± 0.62	3.82 ± 0.47	2.77 ± 0.73	3.5–5.5

for different steps: drying temperature (°C)/ramp/hold (s) (110/15/10), ashing temperature (°C)/ramp/hold (s) (1200/10/15), atomization temperature (°C)/ramp/hold (s) (2100/0/5), and cleaning temperature (°C)/ramp/hold (s) (2300/1/3). A PEL domestic microwave oven (Osaka, Japan), programmable for time and microwave power from 100 to 900 W, was used for total digestion of samples.

Study population

In the present study, the scalp hair samples of boys, age ranged 12–15 years, working in BRW for last 12–36 months, were collected during January 2010 to February 2011. We visited more than 40 workshops in big cities of Sindh (Hyderabad and Karachi), Pakistan, but due to non-cooperative behavior of owners of workshops, only 118 WBs were given consent to provide scalp hair samples. For comparison purpose, boys of same age group residing in the vicinity of workshops (within 50–500 meters) and nonexposed domestic areas (devoid of any industrial activity) were also selected as EBs ($n = 85$) and RBs ($n = 90$), respectively. All WBs were involved in manual laboring, engaged in collecting Pb electrodes from batteries, and smelting them. At the start of the study, the participants' serum ferritin, red blood count, hemoglobin, and haematocrit levels were measured and recorded (Table 1).

In BRW, no environmental control measures are taken to manage Pb exposures in the workplace due to weaker environmental regulations. The effective anti-emission equipments and safety measures put in place by the owners of work shops to protect the workers from exposure to Pb were not carried out. The boys were working in BRW for 6 days in a week, from 8 a.m. to 8 p.m. The municipal and state health authorities were providing no medical care to young age workers. The study protocol was approved by an Ethical Committee and a verbal informed consent was taken from all boys, and parents, while owners of workshops were not cooperated.

Sampling

Scalp samples were collected from WBs, EBs, and RBs of same age group. Scalp hair samples of understudy workers and referent groups were collected from nape of the neck. The hair were tied together from 1 cm of scalp with Teflon thread and cut with stainless steel scissor, and treated as reported in previous work (Kolachi et al., 2012; Afridi et al., 2012). Collected samples were placed in polythene bags, closed with a zipper, and immediately transported to the laboratory and stored. Before analysis, each individual scalp hair sample was cut into approximately 0.5 cm pieces and mixed to make a representative hair sample. Each hair sample was washed with dilute Triton X-100, and then rinsed with distilled water, deionized water, and acetone.

Methodologies

Microwave-assisted acid digestion method

A microwave-assisted digestion procedure was carried out for decomposition of organic matrixes of hair samples. Replicate samples of scalp hair (200 mg) of each study subjects and five replicate samples of CRM sample were directly taken into Teflon PFA flasks (25 mL in capacity). To each flask, 2 mL of a freshly prepared mixture of concentrated nitric acid (HNO_3)–hydrogen peroxide (H_2O_2; 2:1, v/v) was added; the flasks were kept for 10 min at room temperature and then placed in a covered polytetrafluoroethylene container. Flasks were then heated following a one-stage digestion program at 80% of total power (900 W), 6 min was required for hair samples. Thereafter, the digestion flasks were cooled and the resulting solution was evaporated to a semidried mass to remove excess of acid, and then diluted up to 10.0 mL in volumetric flasks with 0.1 M HNO_3. Blanks and standard solutions were prepared in a similar acid matrix. The concentrations were obtained directly from calibration graphs after correction of absorbance for the signal from an appropriate reagent blank. The validity and efficiency of the microwave-assisted digestion method was also checked with conventional wet acid digestion method

Table 2. Lead concentration in scalp hair of referent, exposed, and worker adolescents (boys).

Scalp hair (μg/g)		
Referent boys	Exposed boys	Worker boys
7.25 ± 1.53 (7.0)[a]	10.5 ± 1.40 (10.54)	13.8 ± 2.10 (13.77)

[a]Values in parenthesis are median.

on the same CRMs, as reported in previous works (Kazi et al., 2008, 2009). Statistical analyses were performed using Statistical Analysis System (SAS) software (release 8.01; SAS Institute, Inc., Cary, North Carolina, USA).

Quality control

Calibration was performed with a series of certified standard solution of Pb. The linear range of the calibration curve reached from the detection limit of up to 50 μg/L. The limits of detection (LODs) and limit of quantification (LOQ) for Pb were calculated as $3s/m$ and $10s/m$, respectively, where s is the standard deviation (SD) of the blank (n=9) and m is the slope of the calibration graph. The LOD and LOQ were calculated for Pb as 0.5 and 1.6 μg/L, respectively. The precision of the microwave-assisted acid digestion was expressed as the percentage relative SD of a minimum of nine independent analyses, calculated as <10%. The validity and efficiency of the microwave-assisted digestion method was also checked with conventional wet acid digestion method on same CRM and real samples as reported elsewhere (Kazi et al., 2006, 2008, 2009).

Results

This study shows a clear relationship between environmental and occupational Pb exposure and its incorporation into biological sample (scalp hair).

The mean values of Pb in scalp hair along with median values are shown in Table 2. The level of Pb in scalp hair samples of WBs was significantly higher at 95% confidence interval [CI: 13.4, 14.2] than EBs [CI: 10.2, 10.8] and RBs [6.89, 7.58] μg/g, ($p = 0.01, 0.001$).

Discussion

In industrial societies, sources of Pb exposure, includes: the smelting and refining of Pb, combustion of leaded fuels, the production and disposal of batteries, Pb paints industries, burning of Pb-painted surfaces, and application of pesticides containing Pb-arsenate. Pb battery manufacturing and recycling are now the most significant sources of Pb exposures throughout the world (Gottesfeld and Pkhrel, 2011).

The small-scale Pb battery workshops tend to have high levels of both Pb fume and Pb dust due to lack of ventilation system. To our knowledge, the present study is the first that compares the Pb concentration in scalp hair of adolescent boys, working in BRW and referents from exposed and nonexposed areas, using an analytical technique that provides results with quantification limits of 1.6 μg/L. The WBs were not going to school due to poverty, weakly developed educational systems, lack of enforced legislation and public awareness. The WBs may work whole days, resulting in exhaustion, poor judgment, and subsequent increased physical and emotional risks as reported in other studies (Fee, 2004; Selevan et al., 2003; Lanphear et al., 2005).

The results indicated that the WBs and EBs were at high risk of environmental pollution and had higher Pb levels in their scalp hair samples as compared to RBs (Table 2). Most of the WBs had mild to moderate symptoms of abdominal pain, anemia, muscle pain, irritability, and sleeping disorders, checked by basic health unit (not reported here). In workshops, no use of protective gear (gloves, goggles, or face shields), careless disposal, or storage of leaded materials combined with inadequate sanitation may also increase their vulnerability to Pb-toxicity. The families of WBs have very low socioeconomic status. Some epidemiological evidence suggests that the neurotoxicity of Pb is enhanced in children belonging to families with low socioeconomic status, which are at greater risk (Bellinger, 2008).

Pb–acid batteries contribute to the contamination of all environmental media during their production, disposal, and incineration. It was reported in literature that Pb workers may also absorb it by ingestion either via hand-to-mouth activity or by eating (Hsiao et al., 2001). Due to the absence of effective anti-emission equipments, these small workshops contaminated the working environment and neighboring residential area. In Taiwan, a study reported air Pb levels of 10 μg/m^3 in a kindergarten near a battery recycling plant (Wang et al., 1998). Pb levels in these children reached 150–250 μg/L of blood and these Pb-exposed children had a significantly lower IQ than children living in unexposed areas (Wang et al., 1998).

It was reported in literature about the tendency of control Pb exposures in the workplace or environmental

Table 3. Comparison of lead contents (μg/g) in scalp hair of children of different age group from various parts of the world.

Authors	Age groups (years)	Range	Country
Samanta et al., 2004		8.03	India
Senofonte et al., 2000	10–13	7.37 ± 6.32	Italy
Meng et al. 1998	12–19	3.98–2.56	China
Seifert et al., 2000	6–14	1.61	German
Wilhelm et al., 2002	8–10	0.2–9.9	Germany
Sanna et al., 2003	10–15	3.19 ± 2.54	Italy
Strumylaite et al., 2004	10–13	2.6–3.6	Lithuania
Torrente et al., 2005	12–14	0.32 ± 0.3	Spain
Ozden et al., 2007	11–13	2.41 ± 2.22	Turkey
Ferre-Huguet et al., 2009	12–14	0.58 ± 0.68	Spain
Priya and Geetha, 2010	4–12	1.56 ± 0.18	India
Carneiro et al., 2011	12–18	0.0004–0.7483	Brazil
Zheng et al., 2011	Adolescent residents in e-waste area	14.97	China
	Occupationally exposed worker	40.1	
	Residents in control area	2.94	
Ponzetta et al., 1998		15.7	Indonesia
Sanna et al. 2002	11–16	0.4–75.2 μg/g	Italy
Wang et al., 2009a	6–12	16.6 ± 2.61^{m} 9.6 ± 3.01^{f}	China
Wang et al., 2009b		49.5	Taizhou
Present study	10–15		Pakistan
Exposed WBs		13.8 ± 2.10	
Exposed RBs		10.5 ± 1.40	
Nonexposed RBs		7.25 ± 1.53	

^{f}Female. ^{m}Male.

emissions in several countries. Such reductions have been reported in the United States (Muntner et al., 2005), Canada, Germany, Norway, United Kingdom (WHO, 1995), and Mexico (Flores and Albert, 2004).

The levels of Pb in EBs and WBs exceed the value of 9 μg/g, which is proposed as the level of concern (Esteban et al., 1999; Revich, 1994). While the nonexposed RBs have Pb levels in scalp hair ranged as 6.45–8.5 μg/g, which is above the natural threshold (5 μg/g) for hair Pb concentration (Furman and Laleli, 2000).

The contents of Pb in scalp hair of adolescent workers in the present study were compared with those reported in other studies (Table 3). Our results are consistent with other studies carried out in India and Italy (Samanta et al., 2004; Senofonte et al., 2000), while higher than those values reported in other studies (Carneiro et al., 2011; Ferre-Huguet et al., 2009; Meng, 1998; Ozden et al., 2007; Priya and Geetha, 2011; Sanna et al., 2003; Seifert et al., 2000; Strumylaite et al., 2004; Torrente et al., 2005; Wilhelm et al., 2002) (Table 3).

Our measured Pb concentrations of WBs and ER are lower than occupationally exposed adolescents and those lived in industrial area in china reported by Zheng et al. 2011 (Table 3). In contrast, the nonexposed subjects have lower levels of Pb than our values for RBs. The values of Pb in scalp samples reported by different studies (Ponzetta et al., 1998; Sanna et al., 2003; Wang et al., 2009a, 2009b) are higher than our results for workers and RBs of same age group (Table 3).

In developing countries including Pakistan, the municipal and state health authorities are not taking much responsibility of medical care for the whole population including children of all age groups. The present resulted data indicated that occupational and environmental health standards should be implemented and enforced to control Pb pollution from battery repairing, recycling, and manufacturing operations. Such standards will also reduce the risk to the people, who are living in close proximity to these workshops.

Conclusion

This study underlines that Pb levels in scalp hair may be influenced more by environmental exposure. The levels of Pb in scalp hair samples were measured in three different adolescent (boys) subgroups from two big cities of Pakistan with and without occupational and environmental exposure of Pb. The resulted data indicated that boys working in BRW and living in its vicinity with related to non-EBs were affected with Pb contamination. Occupational and environmental exposure to boys working in the BRW has different health problems. It is very important for community to know the dangers of exposure to Pb for the WBs and other people living in the vicinity of BRW. Of greatest concern are the conditions in which they work and the lack of training of these children in issues of safety increases their risk exposure.

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