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Assessment Of Occupational Exposure To Lead, Cadmium And Arsenic In A Lead-Acid Battery Manufacturing And Recycling Plant In Algeria

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Abstract

Introduction : Plants manufacturing and recycling lead-acid batteries emit this metal and other metal and metalloid particles into the air, which can be transported and deposited on various surfaces, exposing workers and even nearby populations. Occupational metal contamination is a cause for concern because of their potential accumulation in the environment and in living organisms, leading to long-term toxic effects.The aim of this study was to assess Cd, As and Pb levels in the whole blood of 170 people working in a lead battery manufacturing and recycling plant in eastern Algeria, and in that of 50 non-occupationally exposed controls.Metal compound levels were determined using ICP-MS. Lead was the most prominent element in the workers' blood (521.24 µg/L) compared to the controls (23.08 µg/L), confirming that lead exposure is significantly higher compared to other elements. The average and median concentrations of Cd and As in the blood did not exceed the biological exposure indices for both populations. Cadmium levels were significantly higher in the blood of exposed workers compared to the controls. However, there was no significant correlation between blood lead levels and cadmium levels in exposed subjects. For arsenic, although the mean and median values were within the normal range, the maximum and 95th percentile exceeded the normal value. There was also no significant correlation between lead and arsenic concentrations in the blood of workers. The results of this study highlight the alarming working conditions that the employees of this factory face.These conditions lead to significant lead exposure and potentially to other elements such as Cd and As.

Keywords: *lead, cadmium, arsenic, lead poisoning, occupational exposure, lead-acid batteries*

Introduction

Lead-acid battery manufacturing and recycling factories release this metal and other metallic and metalloid particles into the air, which can be transported and deposited on various surfaces, thus exposing both workers and even nearby populations [1]. The presence of these metallic and metalloid contaminants in the emissions and waste of such factories is linked to the composition and the manufacturing and recycling processes of lead-acid batteries.

Workers in the lead-acid battery industry may also be exposed to various toxic elements present as contaminants in mineral Pb, used as catalysts to enhance battery performance, or incorporated into the grid composition for better corrosion resistance. For instance, the lead used in both the positive and negative plates can contain selenium, antimony, arsenic, bismuth, cadmium, copper, calcium, silver, and tin [2, 3]. Consequently, workers may also be exposed to all these elements.

Lead poisoning represents a concerning occupational disease and an ever-present environmental threat to the health of those exposed. According to the World Health Organization (WHO), in 2015, 495,550 deaths and 9.3 million "disability-adjusted life years" (DALYs or years of life lost, adjusted for disability) were attributable to lead exposure due to its long-term health effects. While lead exposure and release rates are carefully controlled in developed countries, they can be considerably higher in low- and middle-income countries. It is in the latter that the highest burden of disease is observed [4].

Lead poisoning is considered the most well-characterized occupational disease. Inhaled or ingested lead can be transported to various tissues and induce adverse effects. The implementation of industrial hygiene and control measures has significantly reduced lead concentrations in workers' blood over the past few decades [5]. This poisoning, particularly in the battery sector, is extremely common worldwide, and Algeria is no exception. However, limited information is available regarding the level of lead exposure among workers in this sector in Algeria and the effects of this metal on the health of Algerian workers.

Cadmium poses a significant health risk to humans, even at very low concentrations ; it interferes with several essential cellular functions. It is a heavy metal that falls between zinc and mercury on the periodic table and exhibits behavior similar to zinc. Prolonged exposure to cadmium results in its accumulation in the body and leads to diseases primarily affecting the lungs and kidneys.

Cadmium increases the concentration of free redox-active metals such as Fe^{2+} and Cu^{2+}, likely by displacing them in various proteins, altering the potential of the mitochondrial membrane, and inhibiting the flow of electrons from reduced ubiquinone to cytochrome c. These free redox-active metals directly enhance the production of hydroxyl radicals (OH) through the Fenton reaction [6]. Oxidative stress occurring in cadmium-exposed cells weakens their defense mechanisms by reducing the activity of antioxidant enzymes and activates proto-oncogenes, leading to cell proliferation. The reduced efficiency of antioxidant mechanisms in cadmium-exposed cells may result from cadmium interacting with zinc, copper, iron, and selenium, resulting in decreased activity of antioxidant enzymes : superoxide dismutase, catalase, glutathione peroxidase [7]. It can be observed that Cd^{2+} diminishes antioxidant enzymes by either replacing metal cofactors or binding to essential thiol groups [8]. Regardless of the mechanism by which cadmium induces oxidative stress in cells, an increase in reactive oxygen species (ROS) occurs, leading to damage and modifications in their structure and metabolism.

Reactive oxygen species (ROS), reacting with the polyunsaturated fatty acids in cell membranes, initiate the process of lipid peroxidation, leading to changes in the membrane gradient. This, in turn, causes the loss of cellular integrity and irreversible damage. These biochemical changes can result in several potentially life-threatening disorders, including Fanconi syndrome, diabetes, kidney failure, cardiovascular disorders, and diseases related to bone absorption [6].

Cadmium can lead to the development of kidney, lung, pancreatic, breast, prostate, and digestive system cancers [9]. Cadmium is classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC) [10].

Arsenic, a naturally occurring metalloid, is ubiquitously distributed in the environment. Although it ranks as the 20th most abundant element in the Earth's crust, it takes the top spot on the list of hazardous and toxic substances for public health [11]. Arsenic's toxicity is associated with the disruption of numerous vital enzymes. Arsenic primarily affects the sulfhydryl group of these enzymes, leading to malfunction in cellular respiration, cellular enzymes, and mitosis [12]. It can block the Krebs cycle and inhibit oxidative phosphorylation. As a result, ATP production decreases, leading to cellular damage. Additionally, arsenic's effect on capillary endothelium increases vascular permeability, causing vasodilation and circulatory collapse [12].

Due to their significant toxicity, arsenic compounds are associated with a wide range of health issues, ranging from gastrointestinal disorders to the development of neoplasms, including skin, liver, kidney, and lymphatic cancer. Exposure to inorganic arsenic is linked to an increased risk of bronchopulmonary, bladder, and skin cancers. Inorganic arsenic compounds are classified as Group 1 human carcinogens by the IARC [13].

The aim of this study was to assess the concentrations of cadmium (Cd), arsenic (As), and lead (Pb) in the blood of a cohort of workers from a lead-acid battery manufacturing and recycling plant, and then compare them to the levels observed in a control group of healthy individuals who were not professionally exposed to these metals.

Materials And Methods

Study Site

This study was conducted at a lead-acid battery manufacturing and recycling company located in the province of SETIF, in eastern Algeria. Worker recruitment took place in the following two units :* Dry and wet battery production unit responsible for producing starting batteries for passenger vehicles, trucks, agricultural vehicles, and machinery. * Second-melting lead production unit for the production of second-melting lead-antimony.

Recruitment Procedure

Workers were approached during a routine medical check-up as part of occupational exposure monitoring at the occupational health department of the University Hospital Center of Setif. Each participant received comprehensive information about the study objectives.

Non-exposed Group : Comprised of 50 healthy individuals, not professionally exposed to lead, with ages comparable to those of the included workers.

Sampling Procedure

Blood samples were collected between 8:00 AM and 8:30 AM after an overnight fast, prior to the start of the work shift, using BD Vacutainer PET tubes - 6 ml - for the determination of trace elements with K2 EDTA additive. Manufacturer's reference: 368381.

To prevent sample contamination, the blood samples were taken outside the factory premises, at the occupational health department, from subjects not wearing their work attire.

The tubes were frozen at -20°C before being transported to the Department of Analytical Sciences, Hubert Curien Multidisciplinary Institute (IPHC), Strasbourg, France, for metal analysis.

Reagents

- Multi-element calibration solution (31 elements) LabKings: IC-MS calibration standard (10 ppm solution in 5% HNO3 traces, containing the following elements: Aluminum, Silver, Beryllium, Boron, Calcium, Cobalt, Copper, Europium, Holmium, Lanthanum, Lithium, Manganese, Nickel, Strontium, Zinc, Antimony, Arsenic, Barium, Cadmium, Chromium, Mercury, Lead, and Selenium): This solution contains all the elements to be analyzed except for tin (Sn).
- Tin calibration solution at 1000 µg/mL in 2-5% Nitric Acid, trace Hydrofluoric acid (TECHLAB Solution, Catalog No. ICP-63N-1).
- Internal standard solution of Indium at 1000 mg/L in 2-5% Nitric Acid (TECHLAB Catalog No. ICP-25N-1).
- High-purity nitric acid from CARL ROTH GmbH.

Analytical Procedures

The concentrations of the calibration standard solutions were selected to cover a wide range of concentrations, ranging from 0.1 µg/L to 800 µg/L, in order to encompass the analyte values of the samples.

Sample Pretreatment : In polystyrene tubes, 250 µL of whole blood were introduced, to which 1 mL of high-purity nitric acid was added. The tubes were placed in a heating block at 60°C for 10 hours, and then the samples were diluted by adding 4 mL of ultra-pure water. An aliquot of 1.5 mL of the diluted digest was taken, to which 15 µL of a 1 µg/L In solution was added.

Instrumental Analysis

The determination of metal concentrations was carried out using the "Triple Quadrupole Inductively Coupled Plasma-Mass Spectrometry ICP-QQQ MS/MS Agilent 8900" spectrometer equipped with reaction/collision cells to reduce polyatomic interferences at the Department of Analytical Sciences, Hubert Curien Multidisciplinary Institute (IPHC), Strasbourg, France (Table 1).

Table 1 : Settings for the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQMS or ICP-MS/MS).

Parameter	Setting
Sample Introduction System	Micromist nebulizer Nebulizer Gas Flow Rate : 1.03 ml/min Nebulizer Peristaltic Pump Speed : 0.1 rps
Radiofrequency Generator	RF Power : 1550W RF Matching : 1,80 V
Gas Flow Rates (for the ICP and the collision/reaction cell)	Plasma : 15 L/min Auxiliary Gas : 0,90 mL/min H_2 : 0,7 mL/min He : 5,5 mL/min O_2 : 20%

Results

The workers ranged in age from 19 to 63 years (40 ± 7.42 years). The age of the control group ranged from 23 to 65 years (42.02 ± 11.70 years). In the exposed worker population, there were 6 women, representing 3.53%, compared to 4 in the non-exposed group, which accounted for 8.16%.

✓ Detection Modes for Isotopes :

Table 2 : Detection modes for isotopes of the elements to be analyzed

Element	Isotope	Detection Mode
As^{75}	75 – 91	MS/MS Detector in "Oxygen Gas" Mode
Cd^{111}	111	MS Detector in "No Gas" Mode
Pb^{206}	206	MS Detector in "No Gas" Mode
Pb^{207}	207	MS Detector in "No Gas" Mode
Pb^{208}	208	MS Detector in "No Gas" Mode

Table 3 displays the average concentrations, medians, and concentration ranges of Pb, Cd, and As in both the exposed and non-exposed populations.

Table 3 : Description of metal concentrations in the studied populations (µg/L)

	Mean (SD)	Median	Minimum	Maximum	Percentiles	
					5	95
UNEXPOSED	n=50					
As	1,7 (1,0)	1,3	0,1	4,7	0,6	4,0
Cd	0,8 (0,7)	0,5	0,01	4,0	0,2	2,1
Pb^{208}	23,1 (15,9)	19,5	3,0	78,6	5,1	68,4
EXPOSED	n=170					
As	2,1 (5,5)	0,9	0,0	56,6	0,2	8,0
Cd	1,1 (1,0)	0,8	0,0	7,1	0,02	2,8
Pb^{208}	521,2 (203,3)	553,6	69,6	1027,0	141,4	799,9

Table 4 demonstrates the variations in metal element concentrations according to their biological reference values (BRV).

Table 4 : Variations in metal element concentrations according to their BRVs

Element (BRV) µg/L	EXPOSED (n=170)		UNEXPOSED (n=50)	
	Normal BRV Number (%)	>BRV Number (%)	Normal BRV Number (%)	>BRV Number (%)
As (<5) [14]	161 (94,7)	9 (5,3)	50 100	0 (0,0)
Cd (<0,7) [15]	164 96,5%	6 3,5%	50 100%	0 0%
Pb (<85)	46 (27,2)	123 (72,8)	50 (100)	0 (0,0)
BRV : Biological reference values from the general population				

In Table 5, we provide a comparison of blood concentrations of the metal elements between the exposed and unexposed populations.

Table 5 : Comparison of metal element concentrations in the two populations (concentrations expressed in µg/L).

	UNEXPOSED n=50	EXPOSED n=170	P
	Mean (SD)	Mean (SD)	
As	1,7 (1,0)	2,1 (5,5)	>0.05
Cd	0,8 (0,7)	1,1 (1,0)	**<0,05**
Pb^{208}	23,1 (15,9)	521,2 (203,3)	**<0.001**
p : t student test			

We conducted a correlation analysis to assess the existence of a relationship between the concentration of each element and that of lead (Table 6). To avoid the occurrence of spurious correlations caused by values that deviate significantly from the others, the Spearman method is employed, which uses the relative rank of the results rather than the values themselves [16].

Table 6 : Correlation of metal element concentrations with blood lead levels in both populations

Element	SPEARMAN Correlation	UNEXPOSED	EXPOSED
As	Correlation coefficient	0,193	0,090
	p (Sig. (Bilatéral))	>0,05	>0,05
	n	50	170
Cd	Correlation coefficient	0,569	0,043
	p (Sig. (Bilatéral))	**<0.001**	>0,05
	n	50	170
Pb [208]	Correlation coefficient	1,000	1,000
	p (Sig. (Bilatéral))	-	-
	n	50	170

Dicussion

Lead

We interpreted the blood lead levels of the workers in relation to the threshold value set at 400 µg/L (according to French labor code). The average blood lead level of the workers was 521.24 µg/L, with a median of 540.5 µg/L. 123 workers, or 72.78%, had blood lead levels exceeding the limit value. This percentage increases to 89.41% (152 workers) when considering the ACGIH biological exposure index, which sets the threshold blood lead level at 200 µg/L [17]. The median and geometric mean of blood lead levels were also above the limit values, reflecting the extent of lead exposure in the workplace.

The blood lead levels found in our study were compared to data reported in the literature for a similar occupational exposure. The results are summarized in Table 7.

Table 7 : Blood lead levels reported in the literature

Auteurs	Country	Industry Sector	N	Blood lead level (µg/L)	
				Mean ± SD (Median)	Range
Kianoush & *al.*, 2013 [18]	Iran	Car battery industry	112	398.9 ±177.4	109 - 894
Akhtar Ahmad & *al.*,2014 [19]	Bangladesh	Lead-acid battery industry	118	652.5 ± 266.6	
Taheri & *al.*,2012 [20]	Iran	Lead-acid battery factory	142	75.9 ± 27.5	26.0-161.0
Raafat & *al.*,2012 [21]	Egypt	Battery industry	57	645 + 54.7	
Nouioui & *al.*,2019 [22]	Tunisia	Battery industry	52	752.6 ± 271.3 (704.0)	332–2080
Himani & *al.*,2020 [23]	India	Battery factory	100	395.0 ± 319.0	
Fenga & *al.*,2006 [24]	Italy	Used lead-acid battery storage facility	50	423.3 ± 151.6	
Bagci & *al.*,2004 [25]	Turkey	Industries des batteries	62	368.3 ± 81	
Basit & *al.*,2015 [26]	Pakistan	Lead-acid battery factory	40	691.7 ± 376.8	250- 1480
Were & *al.*,2014 [27]	Kenya	Battery manufacturing Battery recycling	40 41	470 ± 76 501 ± 96	340–690 32.0–71.0
Ogbenna & *al.*, 2017 [28]	Nigeria	Battery repair	66	(207.5)	182.8–240.8
Patil *et al.*,2007 [29]	India	Battery manufacturing	30	536.3 ± 169.8	258-785
Ghanwat *et al.*, 2016 [30]	India	Battery manufacturing	43	599.3 ± 95.7	

The results of Ahmad et al.'s (2014) study are comparable to ours. The authors found that 84% of lead-acid battery manufacturing workers in Bangladesh had blood lead levels > 400 µg/L, which was attributed by the authors to poor working conditions, inadequate use of personal protective equipment (PPE), and long working hours [19].

In Tunisia, the study by Nouioui et al. (2019) reported higher blood lead levels than ours, with blood lead levels > 400 µg/L for all workers except one. 63.5% of the workers had blood lead levels > 600 µg/L (a level set by OSHA for medical suspension). A total of 10.2% of the workers in this study experienced acute lead poisoning with levels exceeding 1000 µg/L [22].

Cadmium

Cd is naturally present in the Earth's crust and in ocean water. The terrestrial abundance of Cd averages from 0.1 to 0.2 mg/kg. The two main sources of exposure to Cd for the general population are through diet and smoking. In the workplace, the primary exposure situations involve the inhalation of vapors or smoke containing the metal [32].

The cadmium levels we measured were significantly higher in the blood of exposed workers compared to the controls ($p < 0.01$). However, there was no significant correlation between blood lead levels and the blood concentration of exposed workers. Nouioui et al. (2018) conducted a similar study in a battery factory in Tunisia. The authors reported cadmium levels in the hair of workers that were significantly higher than those in the controls ; however, these levels were low compared to those found in other sectors and met the standards applied to a non-exposed population [33]. In a study aiming to assess exposure to metallic elements in a battery recycling facility in France, the authors reported that numerous elements were detectable in the workplace atmosphere. Atmospheric cadmium (Cd) was the most concerning contaminant, with concentrations exceeding the French occupational exposure limit (OEL) of 4 µg/m^3. The authors also noted that the highest urinary Cd values (up to 27.6 µg/g creatinine) were significantly higher than the French Biological Exposure Index (BEI) of 5 µg/g creatinine [34].

Arsenic

Arsenic is a ubiquitous element ; contamination of air, water, and soil by arsenic can occur from natural sources such as volcanic eruptions or anthropogenic sources like mining, non-ferrous metal smelting, and fossil fuel combustion. Arsenic is a toxic element and remains a significant concern for human health as arsenic and its (inorganic) compounds are carcinogenic to humans (Group 1 according to IARC). Contaminated food and water are considered the main exposure pathways for the general population [32].

In our control group, the mean, median, and maximum blood arsenic levels were lower than the normal values for the general population.

However, for the exposed population, while the mean and median were within the normal range, the maximum and 95th percentile exceeded the normal value. Nine workers (5.3%) had high to very high levels, with the maximum blood arsenic level measured in a worker from the "wrapping" workshop, reaching 56.62 µg/L, which is 10 times the normal value. Other workshops where we measured elevated arsenic levels included "deburring," "welding," "smelting" (where operators add other metal elements, including arsenic, to the molten lead), and the "versatile station."

All workers with high blood arsenic levels also had lead levels exceeding 400 µg/L, reinforcing the likelihood that these arsenic contaminations were linked to the workers' occupational activities.

This trend is described in a study conducted in Nigeria in a lead-acid battery manufacturing plant, where workers had significantly higher blood arsenic concentrations than the controls [35]. The same observation is reported in a Tunisian study in a similar type of factory, with significantly higher hair arsenic levels in workers compared to the controls [33].

Conclusion

This study has demonstrated that workers were exposed to lead (Pb), cadmium (Cd), and possibly even arsenic (As). Co-exposure to these toxic elements can pose a major threat to the workers, given the cumulative nature of metal poisoning. The contamination levels found in the workers can be attributed to concerning working conditions, leading to inhalation exposure resulting from significant atmospheric concentrations. Non-compliance with basic personal hygiene rules by some workers exacerbates the risk of lead exposure.

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