Environmental Pollution 200 (2015) 16–23

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Health risk assessment of various metal(loid)s via multiple exposure pathways on children living near a typical lead-acid battery plant, China

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ARTICLE INFO

*Article history:*
Received 17 September 2014
Received in revised form
14 December 2014
Accepted 7 February 2015
Available online 14 February 2015

*Keywords:*
Children
Heavy metal(loid)s
Lead-acid battery
Exposure pathways
Health risks

ABSTRACT

Manufacture of lead-acid batteries is of widespread interest because of its emissions of heavy metals and metalloids into environment, harming environmental quality and consequently causing detrimental effects on human health. In this study, exposure pathways and health risks of children to heavy metal(loid)s (Pb, Cd, As, etc) were investigated based on field sampling and questionnaire. Pb was one of the most abundant elements in children's blood, with an elevated blood lead level of 12.45 μg $dL^{-1}$. Soil/dust and food were heavily polluted by targeted metal(loid)s. Food ingestion accounted for more than 80% of the total exposure for most metal(loid)s. The non-cancer risks to children were 3–10 times higher than the acceptable level of 1, while the cancer risks were 5–200 times higher than the maximum acceptable level of $1.0 \times 10^{-4}$. The study emphasized the significance of effective environmental management, particularly to ensure food security near battery facilities.



## 1. Introduction

Refined lead is the main raw material of lead-acid batteries, which consumed up to 84% of lead consumption (Tian et al., 2014). Previous studies found that the estimated lead emission from lead-acid battery industries accounted for more than 80% before 2001 and 3% after 2001 to the total lead emission in the Greater Cairo area (Safar et al., 2014). With the rapid development of battery industries including manufacturing and recycling (Chen et al., 2009; Gottesfeld and Pokhrel, 2011), China has become the largest producer, consumer, and exporter of lead-acid batteries in the world (Chen et al., 2009; Sun, 2012). Unfortunately, many lead-acid battery factories in China are in operation without a production permission certificate (http://news.xinhuanet.com) and represent a large proportion of local pollution and human lead (Pb) poisoning incidents.

It was reported that Pb poisoning incidents from 2009 to 2013 in China affected more than 5000 children, and a portion of them were related to lead-acid battery industry (Chuang et al., 2008; Gao and Xia, 2011; Ji et al., 2011). Besides Pb, other metals or metalloids such as cadmium (Cd), arsenic (As) and chromium (Cr) could also be largely released, since they are associated elements in lead-containing ores, impurities in lead alloys, or frequently used as additives in the molding and casting processes of the industry (Onianwa and Fakayode, 2000). These toxic ingredients would enter into the environment via soil/dust, drinking water, ambient air and food (Granero and Domingo, 2002; Wang and Stuanes, 2003), and into the body through dermal contact, inhalation and ingestion exposure pathways.

Previous studies conducted around battery-related factories mostly focused on Pb pollution in the surroundings (Chen et al.,

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http://dx.doi.org/10.1016/j.envpol.2015.02.010

2012; Onianwa and Fakayode, 2000), lead exposure of occupational workers (Ahmed et al., 2008; Chuang et al., 2008) or children (Chen et al., 2012; Haefliger et al., 2009; Kaul et al., 1999; Kuijp et al., 2013) living in the vicinities of the plants. However, the exposure and combined health risks from other heavy metal(loid)s such as As, Cd, and Cr were rarely studied. Exposure to these heavy metals and metalloids would result in severe impairment in humans such as kidney dysfunction, lung cancer, or neurological effects (Chiodo et al., 2004; He et al., 2009; Koller et al., 2004). Children are more prone to heavy metal(loid)s poisoning due to child-specific physiological and behavior patterns (Fitzgerald et al., 1998; Fowler, 1993). Children's health-related incidents such as lead or cadmium poisoning have attracted nationwide attention (Gao and Xia, 2011), particularly around lead-acid battery areas (Fan et al., 2010; Hu et al., 2002). Therefore, assessing the aggregated risks of exposure to various heavy metal(loid)s via different environmental media and their main pathways in areas where lead-acid batteries are common would be of great importance for providing a rational basis to protect children's health.

The objectives of the present study were to (1) quantify the concentrations of 12 metals and metalloids in water, food, air, soil/dust around a typical lead-acid plant in China; (2) quantify the exposure levels and contributions from each medium; and (3) estimate children's health risks due to exposure to heavy metal(loid)s from each medium. Hazard quotients (HQ) and the incremental lifetime cancer risk (ILCR), characterizing the non-cancer and cancer risk, respectively (Granero and Domingo, 2002; Mari et al., 2009), were used in the risk assessment. Monte Carlo simulation was conducted (Mari et al., 2009), to determine the inherent uncertainty in predicted risks resulted from exposure assessment.

## 2. Materials and methods

### *2.1. Study area*

A typical lead-acid battery plant located in a suburban area of southeast Hunan province was used as a model. The plant was a typical small private battery manufacturer with several bungalows and workers. Like the other 1800 small private lead-acid battery manufactures in China (accounting for 90% of the total enterprises), some procedures in the selected plant including powder, paste and plate separation processes were conducted without automation and closed operation. The wastewater treatment mainly relied on chemical precipitation, due to the simple facilities. Additionally, no other enterprises or industrial activities were located in the study area, and no highways or heavy traffic volumes existed in the vicinity. There was a primary school situated close to the manufacturing area. The children who attended the school mostly lived near the plant, with a distance of 898 m between the manufacturing area and the residence (ranging from 454 to 1284 m). The raw materials used in the battery plant were not considered in this study.

### *2.2. Sample collection and analysis*

#### *2.2.1. Human behavior pattern survey*

After the approval from ethics committee of the National Center for Disease Control, this research was then conducted, mainly focusing on the children in the primary school. Before the survey and sampling, written informed consents by the participants and their guardians, concerning the behavior pattern survey and the household sampling were obtained from 64 participants, who were native-born and aged 5–8 years old. A questionnaire-based survey was then conducted among the participants to determine the key risk factors, such as dietary behavior, daily activity patterns and lifestyles.

#### *2.2.2. Field sampling*

Blood samples were taken from the 64 participants to characterize the internal exposure level. For each child, 4 mL of cubital fossa venous blood was collected (Liu et al., 2009) and stored at −25 °C until analysis.

18 volunteers were randomly selected to participate in the environmental survey on their families. A total of 18 tap water (drinking water) samples (1 L) were collected in acid-washed polyethylene bottles from the 18 volunteers' families. Another 2 typical samples were respectively collected from kitchen and classroom of the school to truly reflect the water quality consumed by the children. The water samples were stored at −20 °C until analysis after adding two drops of 65% concentrated $HNO_3$.

4 samples from the school and 18 samples (1 kg) from the courtyards of the children's homes were collected from the upper soil layer (0–20 cm) in undisturbed locations, using the established sampling method (Zhang et al., 2010). Additionally, 4 dust samples from the floor and stairs of the school classroom and 18 indoor dust samples from the children's homes were collected using a dust-free brush. Each dust sample was mixed with 4 or 5 sub-samples.

2 and 18 samples of 24-h indoor $PM_{10}$ from the school and volunteers' homes were respectively collected on pre-combusted (500 °C, 6 h) quartz microfiber filters (Munktell In C., Sweden) using an established sampling method (Cao et al., 2014). Another 2 samples outside the school were also sampled. Each sampling process was conducted for 3 days. The particle-loaded filters were stored at 4 °C until analysis.

Duplicate daily foods of the 18 volunteers, which were mostly locally produced, were directly sampled from each family. The food of each child consisted of three meals except soup, which represented the actual amount and type consumed by the child. After the food items in each child's diet were weighed separately, several portions of each food item consumed in one day were combined and blended for freeze-drying and cryopreservation.

#### *2.2.3. Sample treatment and analysis*

After thoroughly thawing and shaking, whole blood samples (1 mL) were digested with a preparation system (Liu et al., 2009). The water samples were filtered using Whatman no.1 filter membranes before concentration analysis. During pre-treatment of the aerosol samples, the entire piece of filter was digested using an established method (Hu et al., 2012). After being air-dried, ground and sieved, the soil and dust powder samples (0.1000 g each) were then prepared with an acid digestion procedure (Zhang et al., 2010). The freeze-dried food was ground and sieved, and then 0.5000 g of each child's food was weighed for acid digestion (Li et al., 2006).

All digested solutions were filtered and diluted to appropriate concentrations for instrumental analysis. The concentrations of Cu, Zn, Co, Cr, Cd, Pb, Ni, Sb, As, Se, Mn and V in all samples were measured by ICP-MS (Agilent-7500a, Agilent Scientific Technology Ltd., USA) under the optimized conditions (Zhang et al., 2010). A solution containing rhodium and rhenium was added online using a Y-type canal as an internal standard and subjected to concentration measurements. The results were quantified with an empirical calibration curve obtained from the analysis of a multi-element calibrations standard material.

Representative reference materials of soil and food, as well as spiked recovery for $PM_{10}$ were included in each related digestion batch for quality control of the analytical procedure. Reagent and analytical blanks and duplicated processing of each digested batch were analyzed to assess the process efficacy. All chemical reagents in the experiments were guaranteed reagents. The instrument and method detection limits for different metal(loid)s ranged from 2.4 to 45.8 ng/g (shown in Table S1, supplementary data). The recoveries of the elements were 89–115%. The relative standard