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Lead identification in soil surrounding a used lead acid battery smelter area in Banten, Indonesia

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Abstract. A used lead acid battery smelter generates particulates containing lead that can contaminate the surrounding environment area. Lead is a heavy metal which is harmful to health if it enters the human body through soil, air, or water. An identification of lead in soil samples surrounding formal and informal used lead acid battery smelters area in Banten, Indonesia using EDXRF has been carried out. The EDXRF accuracy and precision evaluated from marine sediment IAEA 457 gave a good agreement to the certified value. A number of 16 soil samples from formal and informal areas and 2 soil samples from control area were taken from surface and subsurface soils. The highest lead concentrations from both lead smelter were approximately 9 folds and 11 folds higher than the reference and control samples. The assessment of lead contamination in soils described in C_f index was in category: moderately and strongly polluted by lead for formal and informal lead smelter. Daily lead intake of children in this study from all sites had exceeded the recommended dietary allowance. The HI values for adults and children living near both lead smelter areas were greater than the value of safety threshold 1. This study finding confirmed that there is a potential health risk for inhabitants surrounding the used lead acid battery smelter areas in Banten, Indonesia.

1. Introduction

Lead acid battery is one of the supporting components motor vehicle acts as a power supply. Nowadays, automotive industry growth in Indonesia is increasing significantly influences the development of lead acid battery industry. Lead is the main component of the lead acid battery. The high cost production as well as restrictions import of lead by the government had caused recycling of lead acid batteries carried out in many countries including in Indonesia [1]. Several common recycling of lead acid battery in order to meet the factory needs are reduction-oxidation and electrolysis methods [2]. In Indonesia, besides the government licensed lead acid battery smelter plants, there are also other activities such as used lead acid batteries burning in the open air by local people. The latter activities do not use any technologies and facilities smelting which environmental friendly. Both activities process produce the formation of sulfides, named lead slag, gas and particulate matter emissions. The particulate matters contain lead derived especially from anthropogenic activities spread out through the air potentially contaminating soil, water, food and the atmosphere. Soil is one part of the heavy metal cycle. Lead will accumulate in human body tissues through the soil ingestion causing toxicity to human if exceeds the tolerance limit [3]. The amount of lead in soil can indicate present of lead

contamination originating from recycling activities of lead acid batteries. Zeinab Safar *et al* [4] in 2014 examined lead in soil from Awadulla secondary lead smelter in Egypt. About 50 percent of soil samples showed a high degree of lead contamination in the range of 302.275-782.625 mg/kg. The results of this study strongly indicated that there was a potential contamination derived from the smelter that should be further examined [4].

Soil analysis with lead pollutant generated by such activities has rarely been studied by people in Indonesia. Therefore, in this study, an identification lead in soil surrounding both formal and informal lead acid battery smelter areas in Banten, Indonesia was carried out. An examination to investigate the degree of pollution, the daily intake amount of lead as a toxic element and to present health risk assessment for lead through soil exposure for inhabitants living surrounding this used lead acid battery smelter area were also studied. These activities were based on a study of ambient air level concentrations of lead in this area which found were quite high [5] so it became a necessity to examine the environmental contamination caused by this smelter which could be the major source of lead in this surrounding area. The method used in this study is energy dispersive X-ray fluorescence (EDXRF). This method is simple in sample preparation, could analyze elements simultaneously as well as has good capability in measuring samples in low concentration in the range of ppm. Lead has high atomic number can be well measured using this method. The results obtained from this study hopefully can be used as a science based information for the authorities to assess the impact of lead contamination to human in surrounding a used lead acid battery smelter area in Indonesia.

2. Materials and Methods

2.1. Site location

Soil samples were collected not only from a used lead acid battery smelter which has license from Ministry of Environment and Forestry Republic of Indonesia but also from an informal lead smelter. Both of them are located in Tangerang, Banten, Indonesia. The climate in this area is categorized as a tropical zone, with an annual average humidity, temperature and rainfall commonly of 78.7%, 27.7°C and 1922 mm, respectively. Two control samples were collected at 40.5 km from Bogor considered as background area. Figure 1 showed the location of sampling site. A soil sampling standard developed in accordance with United States Environmental Protection Agency (US EPA) was adopted [7]. All experimental steps meet the quality assurance of ISO/IEC 17025:2005 which is implemented in our laboratory.

Figure 1. The location of sampling site in Banten, Indonesia

2.2. Sample collection
Total of 16 soil samples and 2 control samples were taken using a lead free shovel at approximate depth of 0-10 cm (surface) and 10-15 cm (subsurface). The particular samples were collected about 250 grams. Soil samples from formal smelter were taken at a distance of 320 m and 577 m in Southwest direction. Meanwhile the samples from the informal smelter areas were taken at a distance less than 100 m of the smelter in 3 directions: West, North and South. Two samples from South were taken at 30 km from the smelter. All soil samples were then placed in plastic bags and were given a laboratory number. The same procedure was applied to the control samples.

2.3. Sample preparation
Soil samples were placed on plastic tray and were sun-dried for 4-5 days. After drying, clods and large aggregates were crushed and mixed using a glass pestle and mortar. A coning and quartering method was used to obtain about 25 grams of homogenous samples. The samples were pulverized and sieved to reduce particle size of soil to less than 0.074 mm.

2.4. Sample measurement
About 1 g of non-pressed standard reference material (SRM) or soil samples with 3 replicates for each sample were placed in plastic sample holders and loaded into the EDXRF Spectrometer MiniPal 4 (PANalytical, Netherland). A soil sediment application method was developed to analyze the elements in SRM and soil samples. The optimum measurement condition of Lead was measured with parameter measurements as follows: voltage 30 kV, current 150 µA, filter material Al and air as medium. Lead was measured with parameter measurements as follows: voltage 30 kV, current 150 µA, filter material Al and air as medium. The measurement time was 300 seconds. A calibration curve used for the purpose of quantitative analysis was obtained from the measurement of the following reference material; soil 7-IAEA (International Atomic Energy Agency), estuarine sediment-NIST 1646 (National Institute of Standards and Technology), estuarine sediment-NIST 1646a and montana soil-NIST 2711a.

2.5. Quality control
Quality control of the method was checked by measuring RM marine sediment-IAEA 457, then evaluated using verification parameters accuracy and precision which are implemented in the laboratory. Acceptable range of the recovery limit is 85-110% for 0.01% concentration [8]. Laboratory precision parameter is described as %RSD. RSD Horwitz (RSDr) was calculated using this formula:

$$\text{RSD}_r, \% = 2^{(1-0.5\log C)} \qquad (1)$$

where C is the concentration of analyte expressed as dimensionless mass fraction. Accepted values of %RSD are supposed to be in 0.5 up to 2 RSDr [9].

2.6. Assessment of lead contaminations in soil
The potential ecological risk of heavy metal pollutants in the surface soils of this study was evaluated using the ecological risk index as a contamination factor introduced by Hakanson, 1980 [10] using this formula:

$$C_f = \frac{C_m}{B_m} \qquad (2)$$

where C_f= contamination factor of the interested element; B_m=background concentration from this study; C_m= concentration of the element in the sample. Category of C_f values: 0-1=unpolluted to moderately polluted; 1-2=moderately polluted; 2-3=moderately to strongly polluted; 3-4=strongly polluted.

2.7. Human health risk assessment

In this study, human health risk assessment of lead mainly focused only on the soil exposure assessment and risk characterization. During the exposure assessment stage, an average daily intake dose (ADD in mg/(kg.d)) is used to quantify the oral exposure dose of deleterious substances [11]. The ADD through soil ingestion can be calculated using the following formula:

$$ADD = \frac{C.IR.ED.EF}{BM.AT} \qquad (3)$$

The variables C, IR, ED, BM, EF and AT represent heavy metals content (mg/kg), ingestion rate (mg/(kg.d)), exposure duration (day), reference body mass (kg), exposure frequency (age) and average time (day), respectively; the values of these parameters are listed in Table 1 [12, 13]. Ingestion rate (IR) soil values in this activity for adult and children are 150 mg/d and 200 mg/d, respectively [14].

Table 1. Parameters used in exposure assessment

Parameter	Value	
	Adult	Children
Reference body mass (BM)	60 kg	25 kg[*]
Exposure duration (ED)	365 d	365 d
Exposure frequency (EF)	70 a	70 a[*]
Average time (AT)	25550 d	25550 d

Note: [*]Daping *et al*, 2015[14]

Hazard quotient (HQ) or hazard index (HI) is a ratio of ADD to reference dose (RfD) characterizes the health risk of non-carcinogenic adverse effects due to exposure to toxicants calculated by the following formulas:

$$HQ = ADD/RfD \qquad (4)$$

$$HI = \Sigma HQ \qquad (5)$$

The RfD represents a toxicity index of a daily exposure to the population in comparison to a safe level of exposure orally over a lifetime. An index value < 1 is assumed there is no risk for adverse health effects from the ingestion of soil exposed to heavy metal for local residents in an anthropogenic activity area [14]. The health risks for inhabitants in surrounding smelter area resulting from the lead contaminated soil ingestion were assessed based on the index. The oral reference dose (RfD for lead in food is 3.50×10^{-3} (mg/(kg·d)) [15].

3. Results and discussion

3.1. Calibration curve

A deconvolution for fitting the spectral of soil 7-IAEA, estuarine sediment-NIST 1646, estuarine sediment-NIST 1646a and montana soil-NIST 2711a was carried out after running the soil sediment application program to construct a standard curve. Lead, the element of interest, was identified using two line energies, L_α and L_β at 10.5 keV and 12.6 keV, respectively. In EDXRF, the determination of lead in soil when arsenic is present in relatively high concentrations is difficult because the energy of arsenic K_α completely overlaps the lead L_α line. To overcome this obstacle, the accurate lead identification was performed using the ratio of lead L_α and L_β lines by applying line overlap (LOV) program.

The determination of lead in soil using calibration curve of standard reference materials is acceptable elsewhere [13]. To construct the calibration curve, the XRF signal intensity of L_α and L_β lines was plotted against the certified value of lead in each SRM. The Pearson correlation coefficient (r^2 value) was 0.9990.

3.2. Quality control result
To check the accuracy and precision of XRF, RM marine sediment IAEA 457 were examined. The accuracy and precision evaluated gave accuracy and precision were 100% and 0.1% respectively. The recovery values for the concentration of 0.01% were in accordance with the accuracy acceptance criteria [8]. Precision of the reference material fulfilled requirement implemented in the laboratory. It means the performance of EDXRF Spectrometer gave a good agreement with the value of standard material.

3.3. Concentration and contamination factor of lead
Concentrations, depth and distance ratio as well as contamination factor of lead in soil investigated in this activity are shown in Table 2.

Table 2. Summary of concentration, depth and distance ratio and C_f of lead in soil samples

Location	Distance	Direction	Concentration (mg/kg)		SD	Concentration ratio between two depths	C_f max	Category
			Surface (max)	Subsurface (min)	(mg/kg)	ratio		
Formal lead smelter	324 m	Southeast	1784	451	943	4	8	Strongly polluted
	577 m	Southeast	385	238	104	2	2	Moderately polluted
Informal lead smelter	65 m	North	868	159	501	5	4	Strongly polluted
	75 m	North	447	89	253	5	2	Moderately polluted
	50 m	West	1350	195	817	7	6	Strongly polluted
	100 m	West	154	135	14	1	1	Unpolluted to moderately polluted
	75 m	South	2125	171	1382	12	10	Strongly polluted
	30 km	South	192	184	6	1	1	Unpolluted to moderately polluted

From Table 2, the ratios of soil lead concentration samples from surface and subsurface in sampling site near the formal smelter area ranged from 2 to 4. It indicated that the lead contamination in surface was higher than subsurface area which means that the lead contaminations were decreased as the depths increased. It also can be found in the soil from informal lead smelters. Similar results of the lead contamination decreased as the function of depth was also studied by Li, *et al* [17]. Some studies reported, lead does not move to any great extent in soils and unless mixing occurs. It generally concentrated near the surface. Therefore, the lead concentrations in the subsurface soil were not significantly different and almost samples showed similar level. The experimental result indicated that concentrations of lead decreased significantly to the distance from the metallurgical works. It can be seen in the formal lead smelters that the lead concentrations in the surface soil collected near the smelter (324 m) was five times higher than the soil at the distance away from the smelter (577m). The lead concentrations of soil collected from informal lead smelter also showed the similar trends toward

the distances. The lead concentrations from the West direction decreased almost nine times from 1350 mg/kg to 154 mg/kg. From the South direction, the lead concentrations decreased more than eleven times from 2125 mg/kg (75m from the smelter area) to 192 mg/kg (30 km from the smelter area. The results showed that the lead concentrations in surface soil from both formal and informal lead smelters were inversely proportional to the distance from the smelter. Therefore, it can be confirmed that the high lead contamination was originated from the lead smelter [5, 6].

Lead concentration from the surface soil in the formal smelter and informal smelter were 1784 mg/kg and 2125 mg/kg, respectively, exceeding the reference value which in the range 2-200 mg/kg of leads in urban soils [18]. They were also higher than the levels detected in the control soils collected from a background area situated far from industrial activity**.** Control samples taken from Bogor gave concentration of 217 mg/kg which was within reference range. Lead concentration from the formal smelter was found in a significant proportion approximately 9 times higher than the reference and control samples. In general, lead concentration from all direction of informal smelter at a distance < 100 m were also higher 4-11 folds than the reference and control samples. Compared to the previous study by Phing *et al* [19], maximum lead concentration from both formal and informal smelters were higher than that in garden soils in mining area, South China (297 mg/kg).

The lead contamination factor (C_f) in soil from formal and informal lead smelters presented in the Table 2. In addition, $C_{f\ max}$ was 8 for the soil collected at 324 m Southeast of formal smelter. Meanwhile the samples from informal lead smelter at 75m South, 50m West, 65m and 75m North resulted $C_{f\ max}$ values of 10, 6, 4 and 2, respectively. These C_f values indicated that the assessment of lead contamination in soils from formal and informal lead smelters was category: moderately and strongly polluted with lead.

3.4. Human health assessment

Daily intake lead of local population and soil exposure risk characterization for adults and children from the investigated area were presented in Table 3 and Table 4.

Table 3. Daily intake lead of local population via soil exposure in this activity

Location	Distance	Direction	ADD µg /(kg d)			
			Adults	Children	Adults	Children
			Surface soil		Subsurface soil	
Control site	40.5 km	South	0.39	1.57	0.22	0.71
Formal lead smelter	324 m	Southeast	4.46	14.27	1.13	3.61
	577 m	Southeast	0.96	3.08	0.40	1.59
Informal lead smelter	65 m	North	5.31	17.00	0.43	1.37
	75 m	North	1.12	3.58	0.15	0.59
	50 m	West	3.38	10.80	0.49	1.56
	100 m	West	0.39	1.23	0.34	1.08
	75 m	South	2.17	6.94	0.40	1.27
	30 km	South	0.48	1.54	0.46	1.47

The results showed ADD of lead for adults living in 324 m Southeast and 65 m North were 4.46 µg/(kg·d) and 5.31 µg/(kg·d), respectively. The investigated areas showed higher ADD of lead than the report of smelting area in Suxian County, South China which was only 0.776 µg/(kg·d) [14]. The ADD of lead for children living in the same area were 14.27 µg/(kg·d) and 17.00 µg/(kg·d). Other direction of informal lead smelter from the 50 m West and 75 m South gave ADD of lead for children were 10.80 µg/(kg·d) and 6.94 µg/(kg·d), respectively. The ADD of lead for adults and children in both areas indicated the exceeding recommended dietary allowance value which concentration is 3.5 µg/(kg·d). In addition, the ADD of lead for children was 3 folds higher than those of adults due to the

greater amount of soil ingestion in children and the children's weights were lighter. Children are prone to be at the highest risk from intake lead in contaminated soils.

The HI risk characterization was obtained from the sum of Total HQ's at two depths of each distance. The hazard index demonstrated in Table 4 indicated the different HI values for adults and children. The highest value was found in adults and children living in Southeast and North direction at the nearest distance from both lead smelters which were also significant higher than the value of safety threshold in no smelting activity area.

Table 4. Lead in soil risk characterization in this study

Location	Distance	Direction	HQ				HI	
			Adults	Children	Adults	Children	Adults	Children
			Surface soil		Subsurface soil			
Control site	40.5 km	South	0.11	0.45	0.06	0.20	0.18	0.65
Formal lead smelter	324 m	Southeast	1.27	4.08	0.32	1.03	1.60	5.11
	577 m	Southeast	0.28	0.88	0.11	0.45	0.39	1.33
Informal lead smelter	65 m	North	1.52	4.86	0.12	0.39	1.64	5.25
	75 m	North	0.32	1.02	0.04	0.17	0.36	1.19
	50 m	West	0.96	3.09	0.14	0.45	1.10	3.53
	100 m	West	0.11	0.35	0.10	0.31	0.21	0.66
	75 m	South	0.62	1.98	0.11	0.36	0.73	2.35
	30 km	South	0.14	0.44	0.13	0.42	0.27	0.86

This study indicated that the potential health risks for inhabitants in the smelter area are higher than control area. Risk evaluation via incidental direct soil ingestion exposed to heavy metals was considered to be an important part of hazard assessment, especially for young children with regular hand-mouth activity. Based on HI value in this study, children exposed to heavy metals to a greater extent than adults, which may harm brain and nervous system development. This study showed, human exposure to heavy metal in soils might occur directly through the ingestion of soil. Long term lead exposure via soil ingestion poses potential health problems to the inhabitants living in the surrounding of these used lead acid battery smelter areas in Tangerang, Banten, Indonesia.

4. Conclusion

The highest lead concentrations were 1784 mg/kg and 2125 mg/kg resulted from the formal lead smelter and informal lead smelter, respectively. Assessment lead contamination in soils in this study from formal and informal lead smelter were category: moderately and strongly polluted by lead stated in C_f index. The average daily intake value of children in this study from Southeast, North, West and South had exceeded the recommended dietary allowance. The highest ADD value for adults and children were 5.31 μg/kg.d and 17.00 μg/kg.d respectively. The HI values for adults and children living from Southeast, North and West direction at the nearest distance from both lead smelter area were considerably higher than the value of safety threshold. These results could be a fundamental data for local government and could be applied to evaluate the surrounding smelter area throughout the country for reducing the lead pollution in the region.

5. References
[1]   Esquivel-Hernández G, Bolaños-Ulloa P, Navarro-Monge M, Alfaro-Solís R, Sibaja-Brenes J P, Mora-Barrantes J C and Valdés-González J 2012 *J.Waste Management and the Environment* **VI** 251-258
[2]   J Pan, Zhang, Y Sun, Z Wang and Y Yang 2012 *J. Electrochem. Commun* **19** 70–72
[3]   Mackay C A K, Taylor M P, Munksgaard N C, Hudson-Edwards K A, and Burn-Nunes L 2013

*J.Elsevier Environmental Pollution***180** 304-311

[4]   Zeinab S, Mounir W L, Wegdan L and Mohammed H K 2014 *The Journal of field actions***7** 1-8

[5]   Muhayatun S., Diah DL, Rita M, Esrom H, Halimah S, Andreas M and Philip KH 2011 *J.Atmospheric Pollution Research* **2** 190-196

[6]   L Rixson1, E Riani and Muhayatun S2015 *A Scientific Journal for The Applications of Isotopes and Radiation* **11**51-64

[7]   US EPA SESDPROC-300-R3 2014 *Operating Procedur Soil Sampling* Effective Date: Aug 21

[8]   Anonymous 2002 *Guidelines for Single Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals* (AOAC)

[9]   Anonymous2004*Definitions and Calculations of Horrat Values From Intralaboratory Data* [serial   online]   [cited   january10th,   2011];Available   from: URL :http://www.aoac.org/dietsupp6/Dietary-Supplement-website/HORRAT_SLV.pdf

[10]   Hakanson, L1980 *Water Resource Journal***14** 975–1001.

[11]   World Health Organization (WHO)*Evaluation of Certain Food Additives and Contaminants 41*[st] *Report of the Joint FAO/WHO Expert Committee on Food Additives)*(WHO Technical Report)

[12]   United States Environmental Protection Agency (US EPA) 2011 *Risk-Based Concentration TableWashington Agency*(Washington, DC, USA:United States Environmental Protection Agency)

[13]   United States Environmental Protection Agency (US EPA) 1989 *Risk Assessment Guidance for Superfund* Vol. I (Washington DC, USA: Human Health Evaluation Manual Office of Emergency and Remedial Response)

[14]   Daping S, Dafang Z, Dong J, Jingying F and Qiao W 2015*Int. J. Environ. Res. Public Health* **12** 7100-7117 doi:10.3390/ijerph120707100

[15]   United States Environmental Protection Agency (US EPA) 2002 *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites* (Washington, DC, USA:Office of Emergency and Remedial response)

[16]   Dana J D, Alison R K and Neil F 2014 Calibration and Evaluation of an X-Ray Fluorescence Method for the Determination of Lead and Arsenic in Soils *J Environ Anal Chem*.Jreac(2014)1000103

[17]   Li, P., Lin, C., Cheng, H., Duan, X., Lei, K.2015. Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China. *Ecotoxicology and Environmental Safety*113, pp. 391-399

[18]   United States Environmental Protection Agency (US EPA) 2011 Risk Hazard Standards for Lead in Paint, Dust and Soil (TSCA Section 403)

[19]   Phing Z, Huanping L, Zhian L, Bi Zhou and Muuray B M 2014*Multiple Exposure and Effects Assessment of Heavy Metals in the Population near Mining Area in South China* Published online 2014 Apr 11. doi: 10.1371/journal.pone.0094484