Total and Leachable Concentration of Trace Elements in Soil towards Human Health Risk, Related with Coal Mine in Jorong, South Kalimantan, Indonesia

Arie Pujiwati, Kengo Nakamura, Noriaki Watanabe, Takeshi Komai

Abstract—Coal mining is well known to cause considerable environmental impacts, including trace element contamination of soil. This study aimed to assess the trace element (As, Cd, Co, Cu, Ni, Pb, Sb, and Zn) contamination of soil in the vicinity of coal mining activities, using the case study of Asam-asam River basin, South Kalimantan, Indonesia, and to assess the human health risk, incorporating total and bioavailable (water-leachable and acid-leachable) concentrations. The results show the enrichment of As and Co in soil, surpassing the background soil value. Contamination was evaluated based on the index of geo-accumulation, I_{geo} and the pollution index, PI. I_{geo} values showed that the soil was generally uncontaminated ($I_{geo} \leq 0$), except for elevated As and Co. Mean PI for Ni and Cu indicated slight contamination. Regarding the assessment of health risks, the Hazard Index, HI showed adverse risks ($HI > 1$) for Ni, Co, and As. Further, Ni and As were found to pose unacceptable carcinogenic risk ($risk > 1.10^{-5}$). Farming, settlement, and plantation were found to present greater risk than coal mines. These results show that coal mining activity in the study area contaminates the soils by particular elements and may pose potential human health risk in its surrounding area. This study is important for setting appropriate countermeasure actions and improving basic coal mining management in Indonesia.

Keywords—Coal mine, risk, soil, trace elements.

I. INTRODUCTION

COAL is widely utilized as primary energy source due to its availability and cost competitiveness among other fossil fuels [1], [2]. In 2016, coal accounted for 30% of global primary energy consumption and supply 40% of global power generation [3]. Furthermore, Indonesia possessed 40 ktoe of coal resources in 2015 which contributed in providing 27% of national primary energy consumption [4].

Along with concerns about global energy provision, coal is a well-known contributor to various environmental impacts [5]. Contamination of soil with trace elements from coal mine is one of the concerns due to the deliverance of the toxic elements to the environment [6]. Coal deposits contain trace elements, which comprise less than 1% of coal inorganic matter [7]. However, some potentially toxic trace elements also occur in coal organic portions and its mineral phases [8]. Furthermore, the exposure of the sulphide minerals to oxidizing condition may release acid mine drainage (AMD). AMD, containing considerable trace elements, could contaminate the vicinity environment [9]-[12]. In addition, coal dust could adversely influence soil and groundwater quality [13].

The release of trace elements from coal to the environment may result in calamitous health impacts [14]. Considerable research has been performed on the toxicity of trace elements to humans near coal mines. The application of selenium-rich carbonaceous shales or "stone coal" as a soil amendment in Southwest China resulted in selenosis disease due to Se uptake through crops [15]. Arsenic poisoning in a coal mining area in Guizhou Province, China, was described by Zheng et al. [16]. The symptoms were hyperpigmentation, hyperkeratosis, Bowen's disease, and squamous cell carcinoma. Sun [17] also reported evidence of arsenicosis because of coal burning in the same province. Yapici et al. [18] observed that children living around a coal mine in Yatagan Turkey were exposed to dust and soil, which contained Pb and Cd.

In terms of the risk to human health, the toxicity arises as the result of exposure to high value of toxic trace elements. Thus, the toxicity is often determined by the total elemental concentration. However, only certain amount of elemental fractions is exchangeable and soluble in soil. Furthermore, trace elements in the polluted soils are mostly mobile and bound to other soil phase. The solubility, exchangeability, mobility, and binding of the elements influence the absorption of trace elements into human body. Therefore, the bioavailability of the particular element is more suitable to determine the potential risk instead of the total concentration [19]-[21].

Stipulation of trace elements binding applies various approach, e.g. adsorption from a solution by solid phase and desorption from the solid phase. In terms of desorption approach, leaching procedure is commonly used, either single or sequential leaching procedure [21]. Single leaching procedures have been considerably used and established to dissolve a solid phase element related to its bioavailability. The procedure could determine the elemental mobility in

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World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:10, 2017

groundwater and the potential availability of contaminants by various transfer pathways [22]. Water leaching could impersonate pore water, which is describing the mobility of trace elements from soil to groundwater. Soil-to-plants transfer is examined by salt solutions, weak and strong acids, and complexing agent extractants [23]. Acid leaching by hydrochloric acid (HCl) could determine the elution mechanism of heavy metals, which is used to conclude the pathway from soil to direct ingestion [24].

The human health risk assessment of trace elements in soil around coal mines has been widely conducted to determine the potential risk of potential toxic trace elements in particular mining, cities, regions, and countries. The assessment has been performed either using total elemental or bioavailability approach [25]-[29]. However, there is limited study that incorporates the leaching concentration for assessing potential human health risk of trace elements from coal mines. Moreover, environmental assessment of potentially toxic trace elements in soil related with Indonesian mining is widely applied for ore-mining affected area [30]-[32], whereas limited study exists for coal mining environment.

The present study assesses the risk poses by several potentially toxic trace elements in the soil of the Asam-asam River basin, Jorong District, Tanah Laut Regency, South Kalimantan, Indonesia. Jorong District possesses coal deposits where the mines are associated with The Asam-asam River. The coal deposits in the study area have been developed and providing energy source for Indonesian power plant [33]. The assessment was supported by conducting (1) chemical analysis of total, water and acid leaching of As, Cd, Co, Cu, Ni, Pb, Sb, and Zn; (2) soil contamination evaluation, and (3) human health risk assessment.

II. MATERIALS AND METHODS

A. Field Site

The present study was carried out in Asam-asam river basin, Jorong District, Tanah Laut Regency, South Kalimantan Province, Indonesia. It is located at about 120 km south-east of Banjarmasin, the capital of South Kalimantan. The Regency covers 3,631.35 km^2 [34]. The South Kalimantan province has a tropical climate, which consists of dry and rainy seasons. The highest precipitation occurs on December (731 mm). The temperature and humidity are ranged from 200 °C to 350 °C and 80%-83%, respectively [35].

The Asam-asam river is an important environment in the regency due to its association with coal mines and other land uses. The river receives AMD from coal mines [36]. The upstream of the river consists of some creeks, which are located in the mountainous area in Batu Ampar District, the northern border of the study area. In Jorong district, the creeks are incorporating into a big river named Asam-asam and flowing to Java Sea in the southern part. The study took place along the Asam-asam river basin from north to south. The northern part has the higher elevation and hilly surface, consisting of coal mines, plantation, industrial forests, and farming. The southern part is lower and flat, consisting of farming, shrub, fish pond, settlement, and estuary [37]. There is also the coal-fired power plant in the southern part of the study area, which receives coal from its surrounding mines [38].

The coal bearing formation in this area is Warukin formation from Miocene era. Warukin formation consists of conglomeratic quartz sandstone, claystone, and sandy claystone. The lignite dominates the particular coal rank, which has low sulphur and ash content. The southern part of the river basin is associated with Dahor formation and alluvium soils. Lignite, kaoline, and limonite are found in Dahor formation. The alluvium soils dominate the coastal area in the southern part [39], [40].
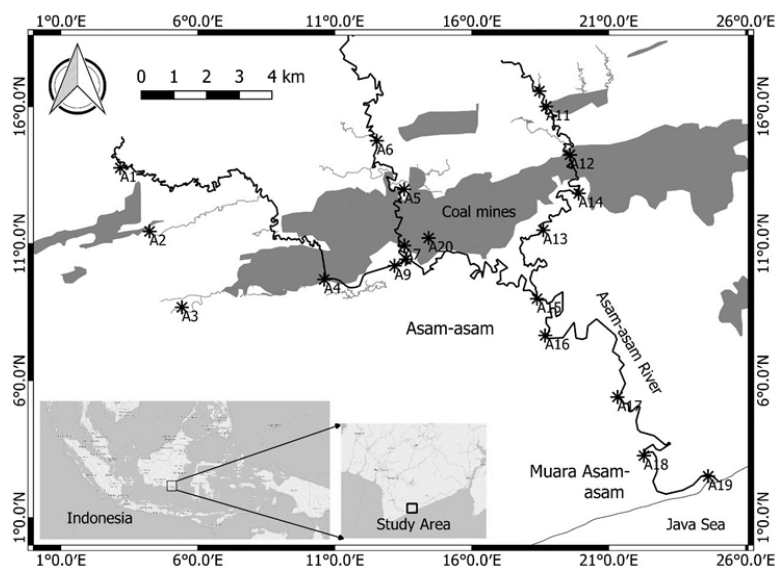

Fig. 1 Sampling location map of the study area

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:10, 2017

B. Sample Collection

A total of 20 top soil samples (0-20 cm depth) were collected from Asam-asam river basin in the early January 2016, representing various land uses. At each soil sampling point, three to five subsamples were collected with a stainless steel hand auger. Randomly collected samples from around each point were thoroughly mixed to obtain a bulk sample. The soil samples were stored in polyethylene bags for immediate transport and storage. In the laboratory, the soil samples were oven dried at 40 °C, pulverized, sieved through a 2-mm mesh, and then stored in sealed polyethylene bags until analyses. Fig. 1 shows the sampling location in the study area.

C. Geochemical Analysis

Bulk analysis was performed to determine the total concentration. The representative samples were ground for 5 min in a planetary ball mill at 450 rpm and then pressed into 32-mm internal diameter pellets using a hydraulic press, operated at a pressure of 200 kN. The selected trace elements were analysed on the Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry (PANalaytical Epsilon 5) following the method of Matsunami et al. [41].

Single leaching procedures were conducted to determine the availability of trace elements, which consist of water leaching and acid leaching. Water leaching analysis is performed to represent the elemental transfer pathway from soil to groundwater. 50 ml of pure water was added to 5 g of soil. The solution was shaken at 200 rpm for 6h, and filtered through a 0.45 μm membrane filter. The acid leaching by HCl represents the elemental transfer pathway from soil to direct ingestion. Acid leaching correlates with the absorbed concentration that would be taken in by directly ingesting soil. This assay represents the maximum potential elution of heavy metals under severe environmental conditions. 1.5 g of soil sample was mixed with 50 ml of 1.0 M HCl, shaken on 200 rpm for 2h, and filtered through 0.45 μm membrane filter [24]. The elements were analysed by inductively coupled plasma mass spectrometry (ICP-MS, ELAN9000, Perkin-Elmer) using Indium (In) as an internal standard for the instrument [42].

The pH and electrical conductivity (EC) were measured from the extracts of water leaching [24]. Soil organic carbon (SOC) was analysed by Walkley and Black's titration method [43].

D. Soil Contamination Evaluation

Soil contamination evaluation was performed by applying Index of Geo-accumulation (I_{geo}) and Pollution Index (PI). I_{geo} evaluates the total concentration results in accordance with the soil background values using (1) [44]:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 B_n}\right) \qquad (1)$$

where C_n is the concentration of an individual element in soil (mg kg^{-1}), B_n is the geochemical background value of a given metal (mg kg^{-1}), and the factor 1.5 is used to account for

potential variation in background values. The background value is obtained from Baharuddin [45] by determining the average result of elemental concentration in the sampling points of BA.04 and BA.06 on that study. The results of I_{geo} are categorized as follows: unpolluted ($I_{geo}\leq0$), unpolluted to moderately polluted ($0<I_{geo}\leq1$), moderately polluted ($1<I_{geo}\leq2$), moderately to heavily polluted ($2<I_{geo}\leq3$), heavily polluted ($3<I_{geo}\leq4$), heavily to extremely polluted ($4<I_{geo}\leq5$), and extremely polluted ($I_{geo}>5$) [46] .

PI is used to evaluate soil contamination in accordance with the applicable regulations. PI was determined by (2) [47]:

$$PI = \frac{C_i}{S_i} \qquad (1)$$

where PI is the pollution index of heavy metal I, C_i is the total concentration of element i (mg kg^{-1}), S_i is the reference value of element i (mg kg^{-1}). This study adopts reference values from the Indonesian toxicity criteria for determining countermeasures of contaminated soil by hazardous waste [48]. The PI results are categorized as no contamination (PI$\leq$1), slight contamination ($1<PI\leq3$), moderate contamination ($3<PI\leq5$), and severe contamination ($5<PI$) [47].

E. Human Health Risk Assessment

The following exposure pathways of trace elements from soil to humans were examined through: (1) soil ingestion, (2) groundwater ingestion, (3) particle inhalation, and (4) dermal contact. Soil ingestion is aimed to describe the ingestion of a combination of soil and outdoor settled dust [49]. For determining a non-carcinogenic risk, receptors were defined as child and adult. In terms of carcinogenic risk assessment, the receptor was determined as resident. The residential receptor was assumed to have an occupancy period of 30 years, consisting of 6 years as a child and 24 years as an adult [49]. Table I describes the exposure criteria of selected trace elements.

To calculate the level of human exposure to trace elements, the following chronic daily intake, CDI (mg kg-day^{-1}) (3) was used [50]:

$$CDI = \frac{C \text{ x SIR x EF x ED}}{BW \text{ x AT}} \qquad (2)$$

where C is the chemical concentration in a particular exposure medium (mg l^{-1}, mg kg^{-1}, mg m^{-3}).

The CDI was modified for each exposure pathway using (4)-(7) [50]:

$$CDI_{s-ing} = \frac{C_{ae} \text{ x SIR x EF x ED}}{BW \text{ x AT}} \qquad (3)$$

$$CDI_{gw-ing} = \frac{C_{we} \text{ x GWI x EF x ED}}{BW \text{ x AT}} \qquad (4)$$

$$CDI_{inh} = \frac{C_s \text{ x InhR x ET x EF x ED}}{PEF \text{ x } 24 \text{ x BW x AT}} \qquad (5)$$

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:10, 2017

$$CDI_{abs} = \frac{C_s \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \qquad (6)$$

where CDI_{s-ing} is the CDI of soil by ingestion (mg kg-day^{-1}), C_{ae} is the acid-leachable concentration of trace elements; CDI_{gw-ing} is the CDI of groundwater by ingestion (mg kg-day^{-1}), C_{we} is the water-leachable concentration of trace elements, CDI_{inh} is the CDI of particle inhalation (mg m^{-3}), C_s is the total concentration of trace elements in soil (mg kg^{-1}), and ABS is the dermal absorption factor (unitless) which defines "desorption of chemical from the soil matrix and absorption of chemical across the skin" [50].

Non-carcinogenic risk is characterized by the hazard quotient, HQ. HQ is determined as CDI divided by a toxicity threshold value. The toxicity threshold value is referred to as a reference dose, R_fD or reference concentration R_fC of the trace elements. The HQ of a single element is determined by (8) and (9) [50]:

$$HQ_{ing} = \frac{CDI_{s-ing} + CDI_{gw-ing}}{R_fD_o} \qquad (7)$$

$$HQ_{inh} = \frac{CDI_{inh}}{R_fD_{inh}} \qquad (8)$$

where HQ_{ing} and HQ_{inh} are the hazard quotient of ingestion and inhalation, respectively. R_fD_o and R_fC_{inh} are defined as the oral reference dose and inhalation reference concentration, respectively.

To determine the HQ of dermal absorption, (10) and (11) are applied to adjust the toxicity threshold values from oral ingestion into dermal absorption [51]:

$$R_fD_{abs} = R_fD_o \times ABS_{GI} \qquad (9)$$

$$HQ_d = \frac{CDI_d}{RfD_{abs}} \qquad (10)$$

where R_fD_{abs} is the adjusted reference dose (mg kg-day^{-1}) for dermal contact, ABS_{GI} is the gastrointestinal absorption factor, and HQ_d is the hazard quotient of dermal absorption.

For contamination by multiple pathways, the Hazard Index, HI is calculated by (12) [50]:

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_d \qquad (11)$$

For $HI < 1$, the exposed population is unlikely to experience obvious adverse health effects. On the other hand, for $HI \geq 1$, the element may have a potential adverse health effect.

US EPA [50] defined carcinogenic risk as the "probability of an individual to develop cancer over a lifetime as a result of exposure to potential carcinogenic elements". Carcinogenic risk is estimated using (13):

$$Risk = CDA \times SF \qquad (12)$$

where $Risk$ is defined as "the unit less probability of carcinogenic risk", and SF is the carcinogenic slope factor (per mg kg-day^{-1}). Risk exceeding 1×10^{-5} is described as unacceptable.

Similar to R_fD for dermal absorption, the slope factor of dermal absorption is calculated from the adjustment of oral ingestion slope factor using (14) [51]:

$$SF_{abs} = {SF_0}/{ABS_{GI}} \qquad (13)$$

where SF_{abs} is the adjusted slope factor (per mg kg-day-1) for dermal absorption pathway and SF_o is the oral slope factor (per mg kg-day^{-1}).

TABLE I
EXPOSURE CRITERIA OF THE SELECTED TRACE ELEMENTS

Initial	Parameter	Unit	Value	Reference
BW	Body Weight for Adult	kg	Adult = 60	[52]
			Child = 15	[49]
EF	Exposure Frequency	days year^{-1}	350	[53]
ED	Exposure Duration	years	Adult = 24	[49]
			Child = 6	
AT	Average Time	days	Non-carcinogenic = ED.365	[50]
			Carcinogenic = 70.365	
ET	Exposure Time	hours	Adult = 24	[51]
SIR	Soil Ingestion Rate	mg kg-day^{-1}	Adult = 0.0001	[54]
			Child = 0.0002	
GWI	Groundwater Intake	l day^{-1}	Adult = 2	[54]
			Child = 1	
InhR	Inhalation Rate	m^3 day^{-1}	Adult = 12.8	[55]
			Child = 7.63	
PEF	Particle Emission Factor	m^3 kg^{-1}	1.36x10^9	[51]
SA	Exposed Skin Surface Area	cm^2	Adult = 4,350	[55]
			Child = 1,600	
AF	Adherence Factor	mg cm^{-2} day^{-1}	Adult = 0.07	[47]
			Child = 0.2	

F. Data Analysis

Basic statistical analyses are performed using Microsoft Excel 2016 software for Windows 7 professional. Data processing calculates minimum *min*, median *med*, maximum

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:10, 2017

max, 1st quartile *Q1*, 3rd quartile *Q3*, average *mean*, standard deviation *SD*, and coefficient of variation *CV*. *CV* is classified as weak variability if *CV* < 10%, and strong variability if *CV* >100%. *CV* ranged within 10-100% is classified as moderate variability [56]. Spatial information is developed by applying QGIS 2.18.4.

III. RESULTS AND DISCUSSION

A. Geochemical Analysis

Soil in the study area was predominantly clay and sandy-clay-loam. The pH range was 2.0 to 7.2, and the average was 4.1. The lowest pH was found in A17 which is associated with palm oil plantation. The soil in the study area tends to be acid, especially those near the coal mines. The low pH near the coal mines signifies substantial supply of free acids, for the example acidic sulphate which is closely related with pyrite as the major mineral of coal. Furthermore, low pH may also be the results of coal mining waste contamination, for instances AMD, coal waste, and coal dust [11], [57]. The pH in this study area was less than that in several previous studies [26], [28], [58]. EC ranges from 0.3 to 156.0 μS cm^{-1}, and the average was 48.9 μS cm-1. The highest EC was found in A12. The conductivity values less than 450 μS cm^{-1} are suitable for plants [59]. The mean SOC varied between 1.0% and 1.6%, and the average was 1.3%. The low SOC showed that mineral soil dominates the soil in the study area instead of the organic soil. The results of pH, EC, and SOC are described in Fig. 2.
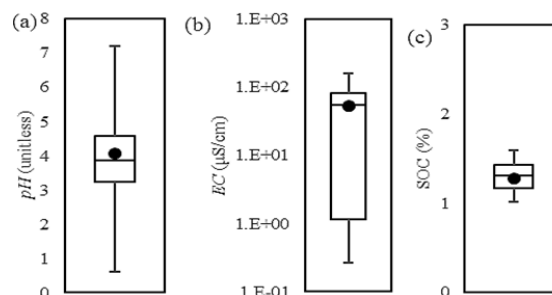

Fig. 2 Box plots of (a) *pH*, (b) *EC*, and (c) *SOC*

The total concentration of soil in the study area was observed. Among all elements, Ni and Zn show the highest concentrations in the range of 14.6 mg kg^{-1} to 533.0 mg kg^{-1} and 21.3 mg kg^{-1} to 186.8 mg kg^{-1}, respectively. Cd has the lowest concentration among all elements, in the range of 0.04 mg kg^{-1} to 0.33 mg kg^{-1} with 13 sample, which is not detectable due to its very low value in the soil samples. Moreover, the farming (A16) has the highest concentration of Cu, Ni, Pb, and Zb. The highest values of As, Cd, Co, and Sb are found in plantation (A1), settlement (A15), dryland farming (A18), and coal mine (A2), respectively. The settlement (A15) has the highest Cd total concentration (0.3 mg kg^{-1}), while the dryland farming (A18) has the highest Co value (59.1 mg kg^{-1}). Furthermore, the mean concentrations of As and Co are surpassing the background value. However, Co is the only element whose background value is beyond worldwide range. All elements have moderate variability, whilst Ni shows strong variability.

TABLE II
GEOCHEMICAL ANALYSIS RESULTS

	As	Cd	Co	Cu	Ni	Pb	Sb	Zn
Total Concentration [1]								
min	7.00	0.04	2.51	9.40	14.58	8.41	0.36	21.31
Q1	12.16	0.07	12.90	17.27	20.56	13.03	0.64	40.85
med	16.25	0.08	21.04	32.45	35.25	16.55	0.73	49.77
Q3	20.09	0.17	32.44	44.97	137.47	19.59	1.03	71.33
max	27.76	0.33	59.12	131.49	533.03	35.29	1.50	186.77
mean	16.38	0.13	24.30	40.35	121.18	17.28	0.80	62.60
SD	5.57	0.10	15.48	33.50	163.21	6.78	0.29	37.52
CV	34.00	73.41	63.71	83.01	134.68	39.25	36.36	59.94
H$_2$O extraction concentration [2]								
min	0.09	0.00	0.02	1.36	0.79	0.57	0.00	0.18
Q1	0.40	0.06	0.21	2.88	6.80	1.26	0.18	16.30
med	0.68	0.23	0.34	3.71	26.14	3.00	0.30	24.75
Q3	1.10	0.50	7.42	5.98	130.57	10.71	0.82	151.81
max	2.86	1.37	38.38	98.29	611.86	76.25	2.31	1,160.42
mean	0.87	0.38	6.25	9.82	124.01	9.84	0.61	160.41
SD	0.67	0.41	10.04	20.81	191.06	16.90	0.67	289.43
CV	77.63	108.31	160.72	211.98	154.07	171.77	109.68	180.44
Acid extraction concentration [1]								
min	0.09	0.000	0.00	0.06	0.03	0.06	0.000	0.07
Q1	0.10	0.001	0.01	0.10	0.09	0.13	0.001	0.13
med	0.11	0.001	0.02	0.14	0.25	0.17	0.001	0.30
Q3	0.12	0.004	0.03	0.26	0.53	0.28	0.002	0.59
max	0.17	0.005	0.12	0.91	2.62	0.40	0.005	0.99
mean	0.11	0.002	0.03	0.24	0.61	0.20	0.002	0.40
SD	0.02	0.002	0.04	0.21	0.83	0.10	0.001	0.34
CV	14.77	87.24	121.81	90.23	135.96	51.83	85.94	85.32

[1]*min, Q1, med, Q3, max, mean, SD* in mg kg^{-1}; *CV* in %
[2]*min, Q1, med, Q3, max, mean, SD* in μg l^{-1}; *CV* in %

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:10, 2017

In terms of acid leaching concentration, arsenic had the least variation among the elements examined, which is ranged within 0.09 mg kg^{-1} to 0.17 mg kg^{-1}. Moreover, the farming (A16) had the highest concentration values of Cd, Ni, and Zn. The highest As and Pb values were found in the dryland farming (A18) and coal mine (A6), respectively. The concentrations of Ni and Zn were more than 100 times of As, Cd, and Sb. Furthermore, half of Cd samples were below the detection limit, as ae result of its very low concentration found in the soil samples.

Water leaching concentration reflects concentrations of trace elements ingested from the groundwater pathway [24]. The results of several assays for Cd, Zn, and Sb were below the detection limit, indicating that the samples could not be extracted well in water. The sample at A11 in the area of the coal mine had the highest Mn (21,461 µg l^{-1}), Co (38.4 µg l^{-1}), Ni (612 µg l^{-1}), Cd (1.37 µg l^{-1}), Zn (1,160 µg l^{-1}), and Sb (2.31 µg l^{-1}). The highest As concentration was found in the settlement (2.86 µg l^{-1}). Pb was the highest (76.3 µg l^{-1}) at coal mine (A14), whilst the highest Cu result (93 µg l^{-1}) was found in the plantation. All samples show strong variability, whereas As shows moderate variability.

Mineral matters in coal could influence the surrounding soil. Pyrite (FeS$_2$) is not only the source of As, but also other trace elements, e.g. Co, Sb, Ni. Moreover, the other minerals e.g. sphalerite (ZnS), ankerite (Ca(Fe,Mg,Mn)(CO$_3$)$_2$), and siderite (FeCO$_3$) contain As, Cd, Pb, Sb, and Zn [60], [61]. Galena (PbS) is the major source of lead. Moreover, the anthropogenic sources of trace elements could also be the result of AMD contamination. AMD could enrich the trace elements in contaminated soils due to the weathering of pyrite which also releasing its occurred trace elements [62]. Masto et al. [13] also observed that atmospheric emissions from coal mining could enrich trace elements in exposed soil. For the case of this study, only As and Co were likely contaminating the soils since they surpassed the background value. Table II describes the geochemical analyses results of total, water leaching, and acid leaching concentration.

B. Soil Contamination Evaluation

I_{geo} introduced by [44] can be used to estimate the extent of contamination by individual elements, compared with the background value [46]. The average results of all elements were classified as "practically unpolluted" with the order based on each average I_{geo}: As > Co > Zn > Sb > Cu > Ni > Pb > Cd. Furthermore, higher elemental accumulation in some locations should be considered separately rather than considering the mean accumulation over the entire basin. The accumulations of Cu, Ni, and Zn were classified as "unpolluted to moderately polluted" in the A15 (settlement) and A16 (farming areas). Moreover, the classification of Co was "unpolluted to moderately polluted" in the A1 (plantation), A8 (shrub), A15 (settlement), and A18 (dryland farming). 11 I_{geo} of As were classified as "unpolluted to moderately polluted". A negative I_{geo} result indicates that the element did not alter the soil when it is compared to the background soil.

The pollution index (PI) evaluation was conducted for As, Cd, Cu, Ni, Pb, and Sb. The mean PI results of the elements are "severe contamination" for Cu, "slight contamination" for Ni, and "no contamination" for Cd, Zn, As, Pb, and Sb. The order of the mean PI of each element was: Cu>Ni> As > Zn > Sb > Cd > Pb. As much as 14 points of Cu and three points of Ni were categorized as "severe contamination". There was "slight contamination" in six points of As, one point of Cu, five points of Ni, and two points of Zn. Furthermore, severe contamination areas were located in coal mines, shrubs, settlement, farming, and mangrove in the estuary. The results of PI showed that Ni and Cu were slightly polluting the soils, based on the reference values. PI could also delineate particular pollution sources that surpassing the reference level, for instances coal mines, agricultural sectors, and settlement. Furthermore, the severe contamination in the estuary as the lowest elevation of the river basin could also be the consequence of contaminant accumulation. Table III describes the results of soil contamination evaluation.

TABLE III
SOIL CONTAMINATION EVALUATION RESULTS

	As	Cd	Co	Cu	Ni	Pb	Sb	Zn
I_{geo}								
BG[1] (mg kg^{-1})	10	1	23	80	292	84	1	71
Min	-1.15	-5.01	-3.79	-3.95	-4.91	-3.91	-2.57	-2.32
Med	0.06	-4.04	-0.72	-2.25	-3.64	-2.93	-1.53	-1.10
Max	0.83	-1.98	0.77	2.07	0.28	-1.84	-0.49	0.81
Mean	-0.02	-3.65	-0.86	-1.95	-2.93	-2.97	-1.51	-0.97
PI								
RV[2] (mg kg^{-1})	20	3	N/A	30	60	300	3	120
Min	0.35	0.01	N/A	2.92	0.24	0.03	0.12	0.18
Med	0.81	0.03	N/A	9.60	0.59	0.06	0.24	0.41
Max	1.39	0.11	N/A	188.33	8.88	0.12	0.50	1.56
Mean	0.82	0.04	N/A	24.95	2.02	0.06	0.27	0.52

[1]BV = Background Value [45]
[2]RV = Reference Value [48]

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:10, 2017
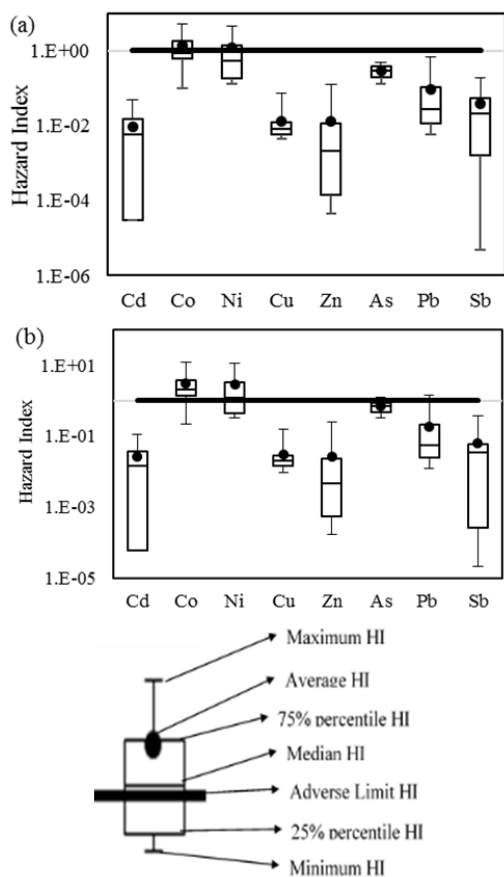
C. Human Health Risk Assessment

Fig. 3 Results of non-carcinogenic risk assessment: (a) adult, (b) child

A non-carcinogenic human health risk assessment was conducted to observe potential non-cancerous effects on the human body due to exposure to these elements. Fig. 3 shows the boxplot result of non-carcinogenic risk assessment. The mean *HI* values of all elements for child and adult were, in order, Co>Ni>As>Pb>Sb>Cu>Zn>Cd. Co and Ni may pose potential adverse risk to adult and child due to their *HI* value, due to their *HI* values which more than 1. The mean *HI* values of Co and Ni are 1.43 and 1.19, respectively. Moreover, A16 (farming), A15 (settlement), A8 (shrub), and A9 (coal mine) were having higher potential non-carcinogenic risks rather than other points.

Different risk levels were assumed for the different groups. Child is the most vulnerable to exposure to non-carcinogenic trace elements. Soil ingestion rate for child (200 mg kg^{-1}) is higher than that for adults (100 mg kg^{-1}) as children have more activities that contribute to incidental ingestion of soil [54]. Child has higher degree of soil adhering to skin following contact, which is also known as the "soil adherence factor" [63].

Among the different selected elements, different predominant pathways generated the non-carcinogenic risk. Ingestion was the predominant route for Sb, Pb, Zn, Cd, and Cu. On the other hand, exposure to Co, As, and Ni was

predominantly through inhalation. Further, the route of exposure may determine the impact of several potential non-carcinogenic risks that may arise from these elements. Lung inflammation is the predominant noncancerous respiratory effect related to toxic soluble Ni compounds [64]. Co is beneficial as a constituent of vitamin B12 but is harmful at high levels, causing toxicity in the lungs and respiratory system due to exposure through inhalation [65], [66]. Inhalation of inorganic As may cause respiratory irritation, nausea, and skin effects [67].

Human health risk assessment for carcinogenic risks was performed only for Ni, Cd, As, and Pb due to the limited availability of oral and inhalation slope factors. The potential carcinogenic risks for Ni and As were unacceptable, whereas the risks for Cd and Pb were acceptable. Mean carcinogenic risk values were, in the order of, Ni (1.1×10^{-3}) > As (3.6×10^{-5}) > Pb (8.14×10^{-7}) > Cd (1.7×10^{-8}). A17 (plantation), A11 (coal mine), A15 (settlement), and A16 (farming) were having higher potential carcinogenic risks rather than other locations. Fig. 4 shows the result of carcinogenic risks.
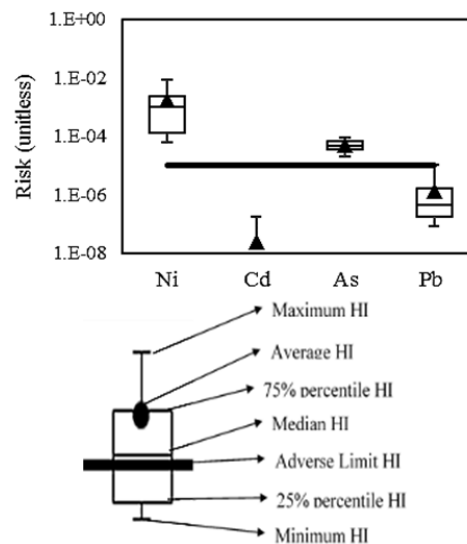

Fig. 4 Results of carcinogenic risk assessment

The breakdown of carcinogenic risk routes also revealed the predominant routes to be different for different elements. Ingestion was the predominant exposure pathway of Ni and Pb, whereas inhalation was observed as the predominant for As. Due to the limited data of particular slope factors, the carcinogenic risk assessment excludes ingestion and dermal contact pathways for Cd, and inhalation pathway for Pb.

Studies on the route of exposure for cancer risk due to Ni have shown evidence supporting inhalation as the main routes of exposure, especially by sulfidic Ni and soluble Ni, which are causative agents of several respiratory cancers, such as lung, respiratory tract, and nasal cancer [64]. Exposure to inorganic As through ingestion may cause dermal and internal cancer, whereas the exposure through inhalation may cause lung cancer [67]. On the other hand, ingestion of inorganic lead is the predominant cause of stomach cancer [68].

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:10, 2017

Inhalation of inorganic Cd was found to be the predominant pathway for lung cancer [69]. From this assessment, the most significant carcinogenic risks were through the exposure to Ni and As.

IV. Conclusion

In this study, a comprehensive environmental assessment of As, Cd, Co, Cu, Ni, Pb, Sb, and Zn in the top soil of a coal mining area and its vicinity in the Asam-asam River basin in South Kalimantan was conducted. The evaluation consisted of geochemical analysis, contamination evaluation, and human health risk assessment. All geochemical analyses revealed As and Co to be the most abundant. The lower I_{geo} for As, Co, Cu, Cd, Ni, Pb, Sb, and Zn is indicating those elements to be insignificantly changed from surrounding undisturbed areas. The results of PI showed slight contamination of Cu and Ni, if referred to the government reference value of contaminated soil. Overall, geochemical analyses and contamination evaluation showed that soil in the study area was slightly contaminated by As, Co, Cu, and Ni.

Even though the contamination evaluation results showed low enrichment and contamination, the study area has significant potential human health risk for specific elements. Children were more susceptible to exposure to trace elements in the soil than were adult to non-carcinogenic risks. Co, Ni, and As may pose more adverse potential non-carcinogenic effects than other elements. The mean HI was in the order of Co > Ni > As > Pb > Sb > Cu > Zn > Cd. In addition, Ni and As may pose higher unacceptable potential carcinogenic risks than other elements. The mean carcinogenic risk for all receptors was in the order of Ni > As > Pb > Cd.

Such information is important to develop the sustainable mining development and take the countermeasure action. Mining waste management is necessary to be applied for the entire mining, especially to minimize the contamination of mining water to the river basin.

Acknowledgment

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