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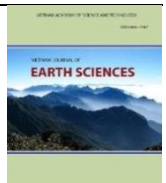

Heavy metal contamination of soil based on pollution, geo-accumulation indices and enrichment factor in Phan Me coal mine area, Thai Nguyen province, Vietnam

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ABSTRACT

Soil samples around the Phan Me coal mine area, Thai Nguyen province, Vietnam had been analyzed for Fe, Mn, Cu, Zn, As, Cd, Hg, Pb and Ni. Single pollution index (PI), geo-accumulation index, enrichment factor have been determined and used for assessing the soil quality. In average by pollution index, the soil heavy metal pollution sequence is Cu(PI=4.2)>Cd(3.5)>Zn(3.1) >Pb(1.7)>Ni(1.3). High concentrations of Cu, Zn and Cd in the soil in the study area are thanks to geo-accumulation and enrichment of the metals in the soil. The soil is from moderately to heavily contaminated by Cu, Zn and Cd: Cu and Zn concentrations are 1.5–2.8 times higher than the ecological risk values, and Cd concentration is about 3.5 times higher than allowable limits. The high concentration of Pb is thanks to moderate geo-accumulation and enrichment of Pb, and the soil mostly has Pb concentration higher than the allowable limit in about 1.7 times. There is a sign that the soil is contaminated by Ni: 22% of the samples have Ni concentration higher than the threshold value, however, the enrichment of Ni is only deficient to minimal. The results of the assessment highlight the need for a comprehensive and detailed study program on heavy metal content in different soil resources in a wider area to identify the magnitude and details of the problem associated with heavy metal contamination for the development of a remediation plan and more effective pollution preventing measures.

Keywords: Soil heavy metal pollution; pollution/geoaccumulation/index; enrichment factor; geochemical background; ecological risk.

1. Introduction

Pollution of soils by heavy metals is a serious environmental problem due to its direct impact on the quality of crop and livestock products as well as the quality of surface water and groundwater. There are different natural and man-made causes of high levels of heavy metals in soils. Natural causes would be the heavy metal accumulation in soils due to the washing and leakage of heavy metals in the natural geological formations during weathering and erosion. The man-made causes are the waste and wastewater sources containing heavy metals that may be dispersed into the environment in one way or another, the mineral mining and mineral processing activities that may disperse heavy metals to the environment, etc.

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Heavy metals in soil and water are a major serious problem for human and had been studied in the USA for more than half of century since 1970 to better understand the potential for food-chain transfer of Cd, Pb, and other potentially toxic trace elements (Holmgren et al., 1993). Deep concern about the food-chain transfer arose at that time was because (i) Cd injured Japanese farm families who had rice grown on Cd-contaminated rice paddy soils (Kobayashi, 1978; as cited by Holmgren et al., 1993); (ii) some children had high Pb levels in the blood at least partially due to Pb in commercial foods as the major food processing source of lead in food is the lead-soldered can (Jelinek, 1982); and (iii) many cities are applying sewage sludge which contains heavy metals on cropland. Holmgren et al. (1993) in their research had obtained the statistical data on heavy metal in soil across the whole USA, which shows that less than 5% of the soil samples across the whole USA (Holmgren et al., 1993) has only Cd greater than the US regulatory standard level (He et al., 2015). It would imply that natural uncontaminated soils by heavy metal in the USA have heavy metal concentrations mostly within the agricultural regulatory standard levels. Nevertheless, due to the serious problem of heavy metals in soil and water to humans, the number of heavy metal soil contamination studies in soil and water is getting greater and greater, especially in developing countries, including Vietnam.

Vietnam is a country with diverse and abundant mineral resources with nearly 5,000 mines and ore spots of about 60 different minerals. Mining and processing of mineral resources have an important position in the national economy as it had contributed about 9.6%–10.6% of total GDP since the year of 2000 (Tran Trung Kien and Pham Quang Tu, 2011). However, the exploitation and processing of mineral resources have been leading to different geological hazards including soil pollution by heavy metals that may cause serious human and property loss consequences. Phan Me coal mine has high-quality coal which well meets the requirement for processing coke. The mine has an annual coal exploitation productivity of 100,000 tons form open mine and 30,000 tons from underground mine (National committee for mineral reserves, 2010). Unfortunately, in 2012, a severe landslide occurred in the mine large and high dump, which buried 20 houses and caused six death casualties.

Regarding heavy metals in the environment in the Phan Me coal mine area, Dang Van Minh (2011) analyzed two soil samples from the paddy field adjacent to Phan Me coal mine and one soil sample from the waste of Phan Me coal mine (Table 1). The waste soil has Cd and Zn concentrations higher than the allowable limits, while only one paddy soil sample has Cd concentration higher than the allowable limits (Table 1). However, the number of samples is neither sufficient for statistical analysis or for determination of pollution and geo-accumulation indices, enrichment factor, geochemical background and reference metal to identify the source of the heavy metal contamination as the mining consequence.

The results showed that there is no difference in heavy metal concentrations between the paddy soil and coal tailing, and both paddy soil and coal tailing samples have Cd higher than the allowable limit.

Table 1. Heavy metals in soil from Phan Me coal tailings and paddy field (Dang Van Minh, 2011)

Metal	Soil from tailings	Paddy soil 1	Paddy soil 2	Allowable limit (MoNRE, 2015) for agricultural soil
Cd	9.60	2.25	1.30	1.5
Pb	31.8	43.2	28.3	70
Zn	540.0	47.0	62.5	200
Cu	13.2	33.8	55.6	100
As	< 0.5	< 0.5	8.7	15

Our overviewing study on heavy metal contamination in Vietnam showed that most studies have a nature of the description of heavy metal concentrations in soil and sediment, of a simple comparison with allowable limits, of the distribution of heavy metal concentrations along spreading pathway, and so on. The assessment indices and special parameters such as pollution and geo-accumulation indices, enrichment factor, geochemical background, reference metal, etc. are rarely applied in studies of heavy metal contamination in soil and sediment in Vietnam, which would inappropriately conclude on the source of heavy metal contamination.

This work attempts to assess the soil quality in terms of heavy metals Cu, Zn, As, Cd, Hg, Pb and Ni by comparison with allowable limits, threshold, and ecological risk metal concentration values, the levels of geo-accumulation and enrichment of the heavy metals in the soil around Phan Me coal mine. Fe and Mn are not concerned in this work since they are characterized by low variability of occurrence and are usually used as a reference element (as cited by Joanna et al., 2018) and they are not specified in the National technical standard QCVN 03:2015/BTNMT (MoNRE, 2015).

Within the research KC.08.23/16-20 in the national important program of science and technology KC08, Phan Me coal mine area is one of the study areas, where heavy metals in the soil are under study, an attempt of application of pollution and geo-accumulation indices, enrichment factor, geochemical background and reference metal to identify the source of heavy metals and their concentration distribution characteristics is carried out. The results of the assessment would assist to make a decision on farther comprehensive and detailed study programs on heavy metal contents in different soil resources in mining areas of Vietnam.

2. Study area, material and methods

2.1. Study area

Phan Me coal mine is located in Giang Tien and Phu Luong district, Thai Nguyen Province on the west side of National Road 3 (Fig. 1) The area where soil sampling has been carried out in the southern Cam village, a small valley on the North-West side of the Tan mountain and in the South of Phan Me open mine (Fig. 1). There are about a hundred households in this valley.

Phan Me coal mine area has an area of about 65 ha, which consists of about 46 ha of open mine in Cam village, Phu Luong district in the north of the Du river and more than 19 ha of the underground mine in Giang Tien town. The open Phan Me mining is nearly completed, while the underground Phan Me mining is underway.

The relief of the mine is from low mountainous with the elevation of about 254 m (the Tan mountain) to valley plain relief of 15–25 m. The main river in the area is the Du River, a tributary of the Cau river and many temporary streams. The Du river is very tortuous, has steep banks, depth of 3–6 m and width of 10–20 m and maximal flow rate of 140 m^3/s, and minimal of 0.65 m^3/s (Thai Nguyen Iron and Steel Joint Stock Corporation, 2017).

The area has a tropical monsoon climate with four seasons with two distinguished seasons: the rainy season from April to October with temperature from 17°C to 36°C and the dry season from November to March of the next year with temperature from 14°C to 26°C. The average annual rainfall (2010–2016) is 1798 mm. The rainfall during the rainy season consists of 91% of the annual rainfall (Thai Nguyen Iron and Steel Joint Stock Corporation, 2017).

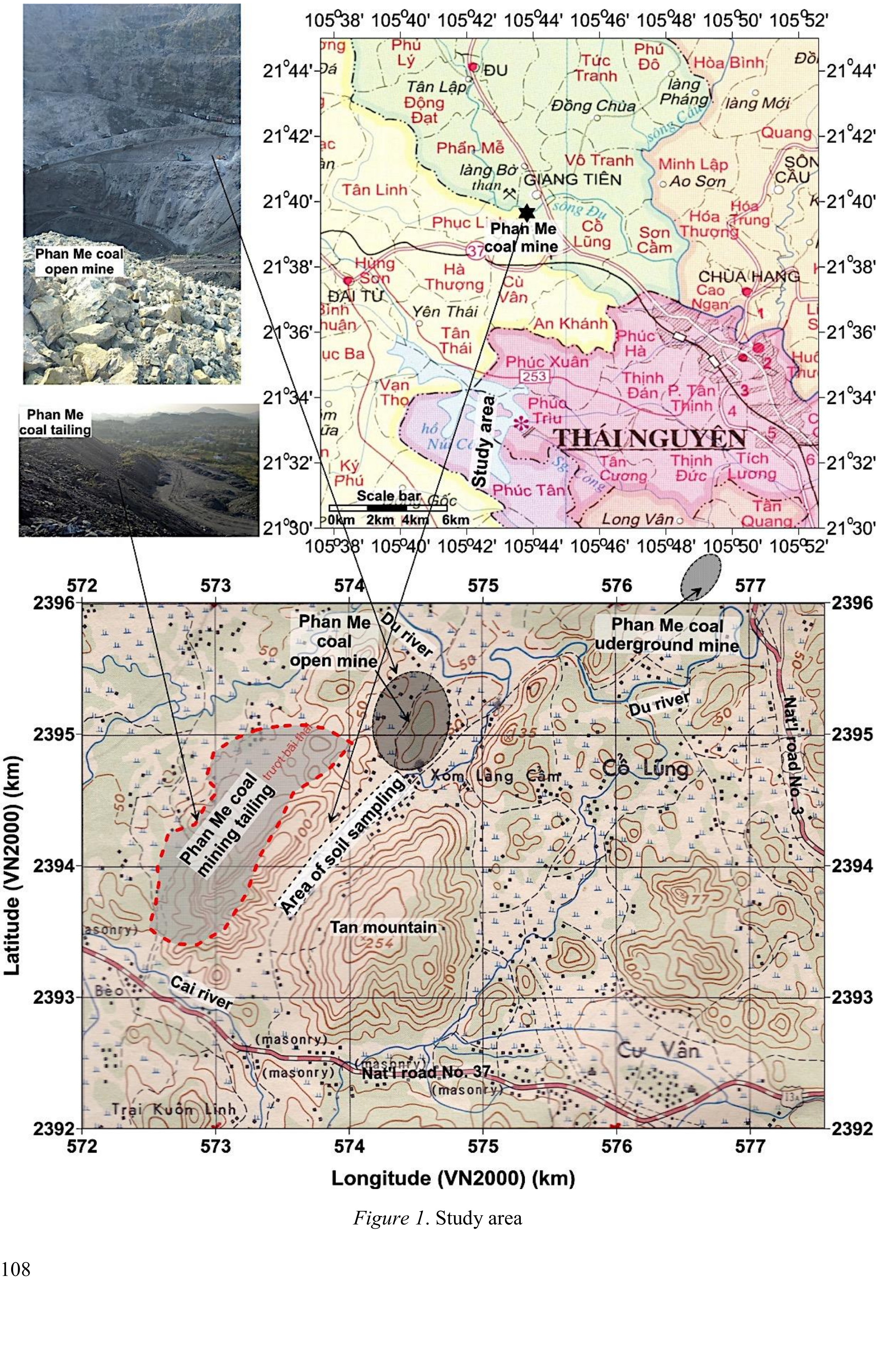

Figure 1. Study area

The geological formation of the coal mine is the Upper Triassic, Lower Van Lang formation (*T_3vl_1*) consisting of sand-siltstone, shale, coal clay, coal and limestone lens. Adjacent to the Van Lang formation is the Lower-Middle Devon, Lower Song Cau formation (*$D_{1-2}sc_1$*) consisting of grey sericite and muscovite shale and sandstone and Ordovician-Silurician, Lower Phu Ngu formation (*O-Spn_1*) consisting of grey quartzite sandstone, Lower Phu Ngu formation (*O-Spn_1*) consisting of grey quartzite sandstone, pyroxene hornblende, shale containing graphite and graphite ore (Fig. 2).

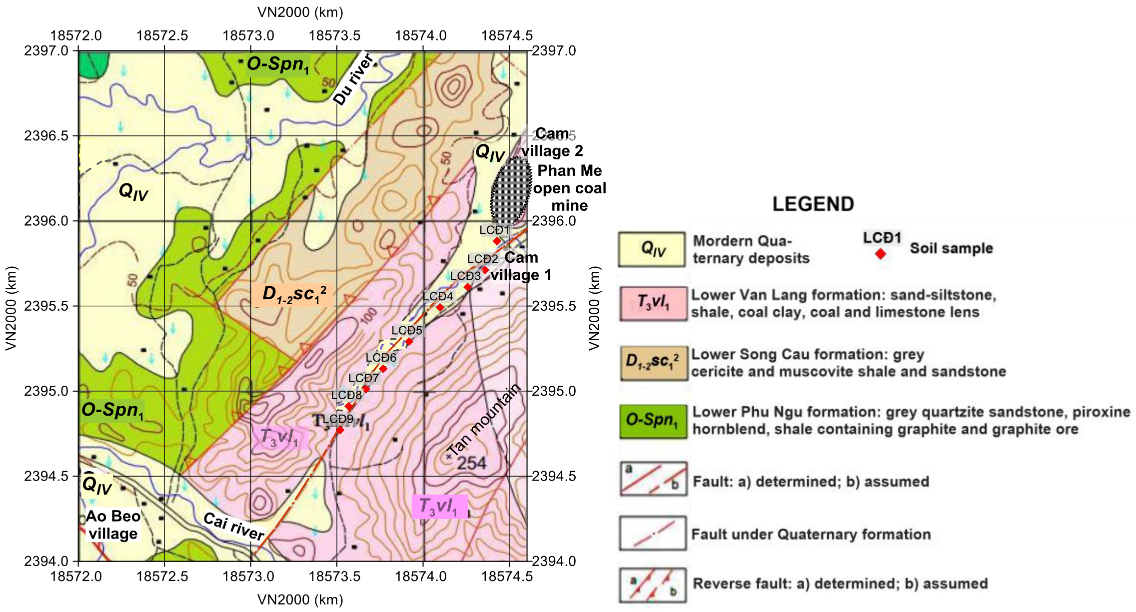

Figure 2. The study area's geological map (Vo Tien Dung, 2017) and soil samples

2.2. Soil sampling and processing for analysis

Soil from the study area had been taken using a spade The soil samples are of spot sample type which is taken from a particular location in accordance with the Vietnam guidance on sampling techniques TCVN7538-2-2005, ISO 10381-2: 2002 (MOST, 2005). All soil samples were taken using a shovel from the top 0.15 m–0.25 m layer. The soil samples are of spot and single (spot-single) sample types which are taken from particular locations.

Within this study, nine spot-single samples have been taken along the valley with an average distance of 160 m. All the samples were taken in the rice paddy field in the 2018–2019 dry season, i.e., in December 2018. The locations of the samples are shown in Fig. 2.

Sampling tools (spade and shovel) were washed with water and dried before the next sampling campaign. The soil sample has a weight of about 1 kg and 0.5 kg, respectively (Alloway, 1995) to ensure 20–50 mg of soil with the sieve opening less than 2 mm. The samples were stored in polythene plastic containers, subsequently, they were air-dried at room temperature in the laboratory, ground in the fine mixture using mortar and pestle before sieving of 2 mm mesh. The processed soil sample is then totally dissolved in the Teflon cup with a mixture of acids HNO_3, HF, and $HClO_4$ in accordance with Jarvis et al. (1992) procedure. Finally 1% HNO_3 is added to the processed dissolved soil sample to get 100 ml of sample solution for analysis.

2.3. Methods of laboratory analysis

Heavy metal elements were analyzed by inductively coupled plasma-mass spectrometer on Varian Ultramass 700 ICP-MS. Inductively Coupled Plasma (ICP) Mass Spectrometry (MS) (ICP-MS) is a multi-element technique that uses an ICP plasma source to dissociate the sample substance into its constituent atoms or ions. The ions themselves are detected by the extracting the ions from the plasma and passing them into the mass spectrometer, where they are separated based on their atomic mass-to-charge ratio by a quadrupole or magnetic sector analyzer (Thermo Elemental, 2001). The analysis detection limit by quadrupole analyzer is from 100 ppt (part per trillion) for Fe to 0.1 ppt for Cd and Pb (Thermo Elemental, 2001) (Table 2). The short-term precision (measurements in the period of 5–10 minutes) is 0.5–2% and long-term precision (measurements in the period of several hours) is 2–4% (Thermo Elemental, 2001) (Table 2).

Table 2. Analysis detection limits and precision by ICP-MS with quadrupole analyzer (Thermo Elemental, 2001)

	Fe	Mn	Cu	Zn	As	Cd	Hg	Pb	Ni
Detection limits (ppt)	100	1	1	10	10	0.1	10	0.1	10
Short term precision	0.5–2%								
Long term precision	2–4%								

Since the used spectrometer has upper detection limits much lower than the threshold and geochemical background values, it well meets this study required analysis accuracy. Certified reference material (JG-1A, Japanese granite) was used to compare the accuracies of the analysis.

2.4. Assessment of factors affecting heavy metal concentration in soil

Geoaccumulation index (I_{geo}) which was proposed by Müller (1969) is an indicator used to assess the presence and intensity of contaminant deposition on soils. The geo-accumulation index is expressed as follows:

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

in which C_n is the measured concentration of the metal element n in soil, B_n is the value of geochemical background of that metal element *n*, and the constant 1.5 accounts for natural fluctuations of the metal element *n* concentration in the environment and very small anthropogenic influence. Müller (1969) has also defined seven classes of the geo-accumulation index and associated soil quality as in Table 3.

Table 3. Classes of geoaccumulation index

Class	Value	Soil quality
0	$I_{geo}<0$	Uncontaminated
1	$0\le Igeo<1$	Uncontaminated to moderately contaminated
2	$1\le Igeo<2$	Moderately contaminated
3	$2\le I_{geo}<3$	Moderately to heavily contaminated
4	$3\le Igeo<4$	Heavily contaminated
5	$4\le Igeo<5$	Heavily to extremely contaminated
6	$Igeo\ge 5$	Extremely contaminated

Single pollution index (*PI*) is used for identifying whether the soil has heavy metal concentration higher than the threshold value:

$$PI = \frac{C_n}{C_{n,thr}} \quad (2)$$

in which C_n is the concentration of heavy metal *n* in soil and $C_{n,thr}$ is the threshold value for heavy metal *n*.

To evaluate the magnitude of ecological risk, a single heavy metal ecological risk ratio (*ERR)* equal to the ratio between the metal concentration and ecological risk metal concentration shall be used.

Reimann and Garret (2005) suggested that the geochemical background (*GB*) value should not be higher than the threshold value, indicating the upper limit of the normal concentration of heavy metal in the soil, and MEF (2007) guided that the GB is used as assessment threshold concentration in areas with a background concentration higher than the threshold value.

Enrichment factor (*EF*) proposed by Buat-Menard and Chesselet (1979) while studying the particulate concentrations of 17 trace metals, Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Sb, Au, Hg, Pb and Th in the marine atmosphere and in the deep waters of the Tropical North Atlantic, as follows:

$$EF = \left(\frac{Metal}{RE}\right)_{soil} : \left(\frac{Metal}{RE}\right)_{background} \quad (3)$$

Where *Metal* is concentration of metal under consideration; *RE* is the concentration of reference element; *soil* is the soil under consideration; *background* is geochemical background soil under consideration. The concentration of heavy metals characterized by low variability of occurrence is used as a reference element, which can be either Fe, Al, Ca, Ti, Sc or Mn (as cited by Joanna et al., 2018).

The soil quality classification is in accordance with the *EF* as indicated in Table 4. Joanna et al. (2018) based on their review showed that several studies have reported that the selection of pollution index to be used is linked with different aims (contamination level, heavy metal origin or ecological potential risk, etc.), and pointed out that I_{geo} and *PI* are used for individual levels of pollution from each of the analyzed heavy metals, and *EF* is used for identification of the source of heavy metals.

Table 4. Classes of enrichment factor

Class	Value	Soil quality
0	$EF<2$	Deficiency to minimal enrichment
1	$2 \le EF < 5$	Moderate enrichment
2	$5 \le EF < 20$	Significant enrichment
3	$20 \le EF < 40$	Very high enrichment
4	$EF \ge 40$	Extremely high enrichment

2.5. Threshold metal concentration values

The soil quality in terms of the heavy metals Cu, Zn, As, Cd, Pb, and Hg is evaluated with the allowable limits specified for agricultural soil in Vietnam national standard QCVN03-MT:2015/BTNMT. Regarding Ni which is not specified in the standard QCVN03-MT:2015/BTNMT, the guideline value specified in the MEF-soil quality guidelines (2007) is used as a threshold value, and high guideline values (ecological risk) specified in the guidelines are used for assessing the soil in the study area (Table 5).

Table 5. Allowable, threshold and ecological risk values for some heavy metals in soil

Metal	MEF Soil Quality Guidelines (2007)		QCVN03-MT:2015/BTNMT - for agr. soil (allowable limits) (mg/kg)	Threshold value used in this study (mg/kg)
	Threshold value (mg/kg)	Ecological risk value (mg/kg)		
As	5.0	100.0	15.0	15.0
Hg	0.5	5.0	Not specified	0.5
Cd	1.0	10.0	1.5	1.5
Cu	100.0	150.0	100.0	100.0
Pb	60.0	750	70.0	70.0
Ni	50.0	150.0	Not specified	50.0
Zn	200.0	400.0	200.0	200.0

2.6. Geochemical background metal concentration values

One of the factors which affect heavy metal concentration in soils is the heavy metal content in the crustal formation from which soils were formed or derived. Karl and Karl (1961) analyzed and interpreted several published data on the metals in some major geological formations of the earth's crust and proposed the following ranges of the metal contents (Table 6).

Table 6. Metal content (mg/kg) in geological formations (Karl K. T. and Karl H. W., 1961)

No.	Metal	Sedimentary rocks		
		Shale	Sandstone	Carbonate
1	Cu	45.0	1.0–9.0	4.0
2	Zn	95.0	16.0	20.0
3	As	13.0	1.0	1.0
4	Cd	0.3	0.01–0.09	0.035
5	Hg	0.4	0.03	0.04
6	Pb	20.0	7.0	9.0
7	Ni	68.0	2.0	20.0

The sediment heavy metal concentration in the study area would be affected by the wide-spreading formation occurrence in the study area as shown in a geological map together with the locations of soil samples (Fig. 2), which is described by Vo Tien Dung (2017):

- The Lower Phu Ngu formation ($O\text{-}Spn_1$) consisting of grey quartzite sandstone, pyroxene hornblende, shale containing graphite and graphite ore;

- The Lower Song Cau river formation ($D_{1\text{-}2}sc_1$) consisting of grey sericite and muscovite shale and sandstone;

- The Lower Van Lang formation (T_3vl_1) consisting of sandstone, siltstone, shale, coal clay, coal and limestone lens.

The geochemical background concentrations of metals in the above-described formations may be taken to be that of sedimentary shale given in Table 5 in accordance with Karl K.T. and Karl H.W. (1961). Kabata-Pendias et al. (1992) also provided the geochemical background of Cu, Zn, Cd, and Ni of sedimentary rock in the European humid zone, the ranges of which are well coinciding with that provided by Karl K.T. and Karl H.W. (1961). The geochemical background of As given by the National Research Council (1977) of 14.5 mg/kg is almost coinciding with that given by Karl K.T. and Karl H.W. (1961). Regarding the geochemical background of Hg and Pb, the site-specific values would be useful. Hg in the sedimentary rocks provided by Aidin'yan et al. (1964) (as cited by William, 1970) is 0.62 mg/kg, and Pb of the sedimentary rocks in the Northeast of Vietnam provided by Nguyen Van Niem et al. (2008) while studying the effect of Pb in the environment on the human health is in the range of 26–28 mg/kg, which are 1.4-1.5 times higher than that summarized by Karl K.T. and Karl H.W. (1961). Based on that, the selected values of the geochemical background used for obtaining I_{geo} and *EF* for the soil in the study area are given in Table 7 along with the reference values by the authors.

Table 7. Geochemical background concentrations (mg/kg) of heavy metals for the study area

Authors	Cu	Zn	As	Cd	Hg	Pb	Ni
Karl K.T. & Karl H.W. (1961)	45	95	13.0	0.30	0.40	20	68.0
Kabata-Pendias et al. (1992)	40	80–120		0.22–0.30		18–25	50–70
National Research Council (1977)			14.5				
Aidin'yan, Troitskii, Balavskaya (1964)					0.62		
Nguyen Van Niem et al. (2008)						26–28	
Selected for use in this study	45	95	13.0	0.30	0.62	27	68.0

3. Results

Most of the taken soil samples (88.9%) in the Phan Me coal mine area, Thai Nguyen province have Cu and Zn concentrations much higher than threshold values, 66.7% and 44.4% of soil samples have Cd and Pb concentrations higher than threshold values, respectively. Only 22.2% of soil samples having Ni higher than the threshold (Table 8, 9). The concentrations of Cu, Zn, Cd, Pb, and Ni are plotted and presented in Fig. 3-7, respectively, together with the threshold level and ecological risk level. The soil samples also have Cu (88.9% of samples) and Zn (55.6% of samples) concentrations much higher than high guideline values, i.e., currently are under ecological risk. Table 8 presents the minimal, average and maximal soil metal concentrations and values of *PI* and *ERR*.

Table 8. Metal concentrations (mg/kg) in soil in area around Phan Me coal mine

Sample	Cu	Zn	As	Cd	Hg	Pb	Ni
Threshold:	100	200	15	1.5	0.5	70	50
% higher than threshold:	88.9	88.9	0.0	66.7	0.0	44.4	22.2
LC-Đ01	423.3	300.1	4.22	0.10	0.01	57.26	24.63
LC-Đ02	289.8	611.7	14.06	5.30	0.03	116.99	63.18
LC-Đ03	333.3	414.2	1.09	3.20	0.01	53.98	40.48
LC-Đ04	84.2	52.1	2.15	0.10	0.02	3.80	24.02
LC-Đ05	356.5	455.9	9.14	2.70	0.02	87.13	43.91
LC-Đ06	311.5	513.0	7.58	4.25	0.02	85.49	51.83
LC-Đ07	208.7	233.2	1.62	1.65	0.02	28.89	32.25
LC-Đ08	220.3	254.0	5.65	1.40	0.02	45.46	33.96
LC-Đ09	334.0	484.4	8.36	3.48	0.02	86.31	47.87
Average	284.6	368.7	5.99	2.46	0.02	62.81	40.24
Standard deviation	100.0	173.0	4.25	1.80	0.01	34.71	12.95

Table 9. Average and maximal soil metal concentration, *PI* and *ERR*

Metal:	Cu	Zn	As	Cd	Hg	Pb	Ni
Threshold (mg/kg)	100	200	15	1.5	0.5	70	50
	Concentration						
Min. (mg/kg)	84	52	1.1	0.10	0.01	3.8	24.0
Max. (mg/kg)	423	612	14.1	5.30	0.03	117.0	63.2
Avg. (mg/kg)	285	369	6.0	2.46	0.02	62.8	40.2
	Pollution index (*PI*)						
Min.	0.8	0.3	0.1	0.1	0.0	0.1	0.5
Max.	4.2	3.1	0.9	3.5	0.1	1.7	1.3
Avg.	2.8	1.8	0.4	1.6	0.0	0.9	0.8
Number of samples with *PI*>1	8	8		6		4	2
% of samples with *PI*>1	88.9	88.9		66.7		44.4	22.2
	Ecological risk ratio (*ERR*)						
Min.	0.6	0.1	0.0	0.0	0.0	0.0	0.2
Max.	2.8	1.5	0.1	0.5	0.0	0.2	0.4
Avg.	1.9	0.9	0.1	0.2	0.0	0.1	0.3
Number of samples with *ERR*>1	8	5					
% of samples with *ERR*>1	88.9	55.6					

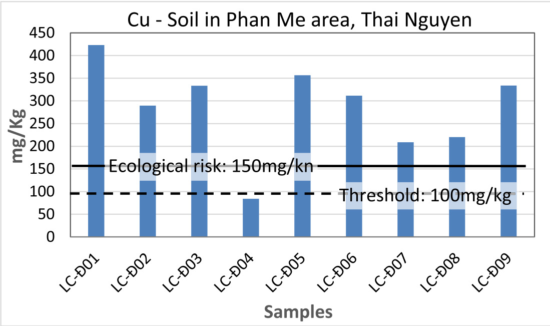

Figure 3. Cu concentration in soil samples

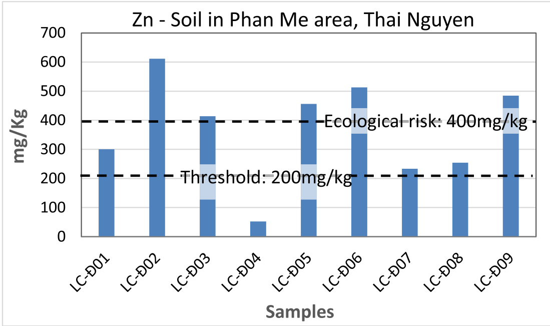

Figure 4. Zn concentration in soil samples

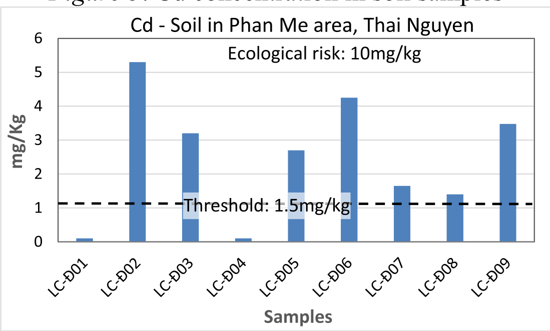

Figure 5. Cd concentration in soil samples

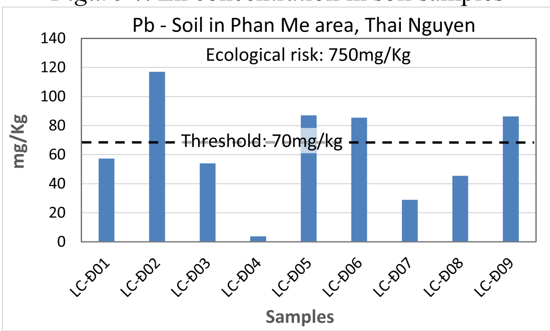

Figure 6. Pb concentration in soil samples

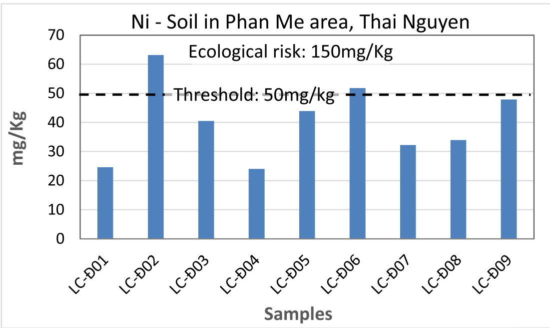

Figure 7. Ni concentration in soil samples

Metal geoaccumulation and enrichment in soil in the study area

Metal geo-accumulation index and enrichment factors in the soil in the study area have been determined and the statistics are shown in Tables 10 and 11, respectively, along with with the contamination I_{geo} classes and enrichment level classes. Similarly to the *PI* and *ERR*, most of the samples are moderate to heavy contamination by Cu, Zn, Cd and Pb in term of I_{geo} class, and moderate to significant enrichment in term of enrichment class. Table 12 summaries the soil heavy metal in respect to threshold level. It would emphasize that the high concentrations of the listed heavy metals in the soil are due to geo-accumulation and enrichment. Based on the *PI*, *ERR*, I_{geo} and *EF* the following sequences are observed:

- Average *PI*: Cu(*PI*=4.2) > Cd(3.5) > Zn(3.1) > Pb(1.7) > Ni(1.3);
- Percentage of samples with *PI* > 1: Cu(88.9%) = Zn(88.9%) > Cd(66.7) > Pb(44.4) > Ni(22.2);
- Average *ERR*: Cu(*ERR*=2.8) > Zn(1.5);
- Percentage of samples with *ERR*>1: Cu(88.9%) > Zn(55.6%);
- Average I_{geo}: Cu(I_{geo}=2.0) > Cd(1.6)> Zn(1.1);
- Higher than moderate contaminated: Cu(88.9%) > Zn(88.9%) > Cd(77.8) > Pb(44.5);
- Average *EF*: Cd(*EF*=9.3)>Cu(8.0) > Zn(4.7) > Pb(2.8);
- Moderate to significant enrichment: Cu(88.9%) = Zn(55.6%) > Cd(77.8) > Pb(66.7).

Table 10. Statistics of geoaccumulation index of metal in soil in the study area

I_{geo} class	Cu	Zn	As	Cd	Hg	Pb	Ni
Min.	0.3	-1.5	-4.2	-2.2	-6.5	-3.4	-2.1
Max.	2.6	2.1	-0.5	3.6	-5.0	1.5	-0.7
Avg.	2.0	1.1	-2.1	1.6	-5.7	0.2	-1.4
	Number of samples						
0-Uncontaminated (uncon.)		1	9	2	9	2	9
1-Uncon. to moderately con.	1	2				3	
2-Moderately contaminated (con.)	2	5		2		4	
3-Moderately to heavily con.	6	1		3			
4-Heavily contaminated				2			
	Percentage of samples						
0-Uncontaminated (uncon.)		11.1	100.0	22.2	100.0	22.2	100.0
1-Uncon. to moderately con.	11.1	22.2				33.3	
2-Moderately contaminated (con.)	22.2	55.6		22.2		44.5	
3-Moderately to heavily con.	66.7	11.1		33.4			
4-Heavily contaminated				22.2			

Table 11. Enrichment factor of metal concentration in soil in the study area

Enrichment Factor	Cu	Zn	As	Cd	Hg	Pb	Ni
Min.	1.1	0.3	0.1	0.2	0.0	0.1	0.2
Max.	18.5	7.4	1.0	18.2	0.0	4.2	1.0
Avg.	8.0	4.7	0.5	9.3	0.0	2.8	0.7
Enrichment class	Number of samples						
0-Deficiency to minimal enrichment	1	1	9	2	9	3	9
1-Moderate enrichment	2	2		2		6	
2-Significant enrichment	6	6		5			
Enrichment class	Percentage of samples						
0-Deficiency to minimal enrichment	11.1	11.1	100.0	22.2	100.0	33.3	100.0
1-Moderate enrichment	22.2	22.2		22.2		66.7	
2-Significant enrichment	66.7	66.7		55.6			

Table 12. Summary of soil heavy metal in respect to threshold level

Sample	Cu	Zn	As	Cd	Hg	Pb	Ni
Threshold	100.0	200.0	15.0	1.5	0.5	70.0	50.0
% higher than threshold	88.9	88.9	0.0	66.7	0.0	44.4	22.2
Average	284.6	368.7	5.99	2.46	0.02	62.81	40.24
Standard deviation	100.0	173.0	4.25	1.80	0.01	34.71	12.95

4. Discussions

Based on I_{geo}, the soil in the area is mostly from moderately to heavily contaminated in Cu, Zn, and Cd. This is well corresponding to *PI* that the soil is contaminated in Cu, Zn, and Cd, however with additional information that the contamination level is moderate to heavy. Based on the *EF* the metals Cu, Zn and Cd are mostly from significant to moderate enrichment. This would allow thinking that the source of Cu, Zn, and Cd in soil contamination in the study area is most likely from the sedimentary rock.

Regarding Pb, the percentage of Pb contaminated and uncontaminated are approximately equal. The Pb contamination level is moderate both in terms of I_{geo} and *EF* and is well corresponding to *PI*, the maximal value of which is only 1.7.

The soil is not contaminated in As, Hg and Ni as the values of *PI* are less than 1, I_{geo} are less than zero and *EF* are much less than 2.

Among the metals under consideration, Cu and Zn are of high concentration in the soil and have an ecological risk level, the *ERR* of which are about 2 and 1, respectively.

The preliminary study results in this work suggest that the soil in the study area naturally is of high concentration of Cu and Zn, up to the level of ecological risk. Meanwhile, Dang Van Minh (2011) made a statement that the soil mining areas in Thai Nguyen province are generally contaminated by Zn, especially in the iron-ore waste tailings. Since the Phan Me coal mine study area is far from iron ore mines in Thai Nguyen, the source of Zn soil contaminations cannot be entirely from the iron ore bearing formation.

Comparing with the results of Dang Van Minh (2011), the soil Cd concentration in both works is more or less the same tendency, Zn concentration is not completely the same tendency, however, Cu concentration is of an opposite picture: the analyzed soil samples by Dang Van Minh are not contaminated by Cu and have Cu much lower than the allowable limit.

The results of the assessment based on the soil samples in Phan Me coal mine, Thai Nguyen province, Vietnam highlight the need for a comprehensive and detailed study program on heavy metal content in different soil resources in a wider area to identify the magnitude and spatial distribution of heavy metals. In the study, the geochemical background concentrations of metals of similar geological formations of published references are used. The actual geochemical background concentrations of metals in the geological formations in the study area, i.e. the Lower Phu Ngu formation ($O\text{-}Spn_1$), the Lower Song Cau formation ($D_{1\text{-}2}sc_1$) and the Lower Van Lang formation ($T_3\text{-}vl_1$) need to be determined to ensure more reliable results.

5. Conclusions

High concentrations of Cu and Zn from moderate to heavy contamination and from moderate to significant enrichment in the soil in the Phan Me coal mine area are thanks to accumulation and enrichment. The soil Cu and Zn concentrations are higher than the threshold and ecological risk values. The high concentration of Cd from moderate to heavy contamination is thanks to the accumulation and enrichment of the metal in the soil. The heavy metal contamination source is mostly natural, from the origin of sedimentary rocks.

A more comprehensive program of soil sampling and analysis of Cu and Zn is needed to be carried out for Phan Me coal mine area in particular and in a wider area in Thai Nguyen province in general since the results of this study have shown an ecological risk of Cu and Zn concentration in the soil. Besides, a detailed effect of high Cu and Zn concentration on the ecological environment is worthwhile to be studied.

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