



## Assessment of heavy metal pollution in abandoned Giap Lai pyrite mine (Phu Tho Province)

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Received 30 March 2017. Accepted 31 May 2017

### ABSTRACT

Giap Lai pyrite mine had been exploited in the period 1975 - 1999, and abandoned after the mine became closed. This work is conducted with the aim to evaluate the impacts of the abandoned mine to the environment. 23 surface water, 15 ground water and 20 soil samples from the mining area were collected for experiments. Acid production potential and metal leaching of waste materials from tailings were tested. Results show that acid rock drainage (ARD) in the old mining area still occurs, with sulfide-rich tailings and waste rocks being sources of ARD, causing elevated metal concentrations in downstream water bodies. Surface water shows significant pollution of Fe, Mn, Ni and partially As. In the rainy season, the percentage of surface water samples having low pH values as well as metal contents in samples is higher than in the dry season. Metal concentrations in ground water are generally low, but many samples have low pH values, indicating the influence of the ARD. The geo-accumulation index reveals that soil from mining area is moderately contaminated with Ni, Cu, Hg and partially As. Most of the polluted samples are located near old mining pits, waste dumps and tailing ponds. The study also shows that negative effect of Giap Lai pyrite mine on the surrounding water and soil has been ongoing. However, no post-closure remediation measures have been applied at the mine, so there must be appropriate solutions for the acid mine drainage treatment before its being discharged to the environment. Given the facts revealed by this study, it is recommended that the Environmental Protection Law should be fully implemented at mining sites not only during the exploitation but also after their closures.

*Keywords:* pyrite mine, abandoned mine, acid drainage, metal pollution.

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### 1. Introduction

Mining and mineral processing can cause many negative impacts on the environment. The formation of acid mine drainage (AMD) and acid rock drainage (ARD) and associated contamination has been described as the largest environmental problem in sulfide-bearing

mines (INAP, 2009). The generation of acid is due to oxidation of sulfide minerals existing in ore, especially pyrite ( $\text{FeS}_2$ ), when they exposed to air and water. Already formed acid is able to dissolve metals and these contaminants, once dissolved, can migrate to local surface water causing environmental pollution. These processes occur during the operation of a mine and can continue for a long

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time, even hundreds of years after the mine closing (Ziemkiewicz et al., 1991). Due to the impact of acid mine drainage and heavy metal pollution, water quality, especially mine land usually was seriously degraded, even impossible to recover and most of the land so often become fallow.

Up to now, in the world literature, there are a huge number of publications on abandoned mines. Many countries have special agencies or programs for research of closed mines (EPA, 2000; MCMPR/MCA, 2010; Mhlongo and Amponsah-Dacosta, 2015; Newton et al., 2000).

In Viet Nam, studies of the post-mining environment are limited. Recently, there is only one report by Tarras-Wahlberg and Lan (2008) on the post-mining environment at Giap Lai pyrite mine. According to these authors, at Giap Lai pyrite mine the ARD is still leaking and metal concentrations in affected surface waters have been increased since the mine closure, suggesting that the impact is becoming progressively serious. The authors also suggest that the present situation is due to the failure in post-mining management.

Mining of pyrite in Giap Lai occurred during the period 1975-1999 and had been closed since 1999. Currently, the old mining pits have turned into acid lakes, and acid drainage continues to form from waste rock dumps and tailings ponds, causing pollution of some heavy metals (Tarras-Wahlberg and Lan, 2008).

Environmental pollution in the Giap Lai mining area has caused anxiety among the people and led to numerous complaints. Pollution is believed to be the main cause in rising fatal diseases in the commune in the recent years.

This paper presents new findings of acid rock drainage phenomenon and heavy metals pollution in the abandoned Giap Lai pyrite mine area to provide the scientific basis for the management of the closed mines and mining environmental protection in general.

## 2. Study area

Giap Lai pyrite mine locates in Giap Lai commune, Thanh Son District, Phu Tho Province, about 80 km northwest from Ha Noi (Figure 1). The area is a valley-shaped running in the northwest - southeast direction at an altitude of about 70 m, among low hills, which reach 200-400 m high. The mining area is drained by Dong Dao stream, which empties into the Bua River about 6.5 km to the northwest.

Like all of North Vietnam, Giap Lai is located in the tropical monsoon climate. There are two distinct seasons: The rainy season coincides with the hot season starting from April to the end of September, the average temperature is from 27°C to 31°C and the highest is 30°C - 39°C; The dry season starts from October to the end of March next year, the average temperature is 20°C - 22°C and the lowest is 6°C - 15°C. Annual rainfall is about 2500 mm, mainly concentrated in the rainy season, especially June, July and August.

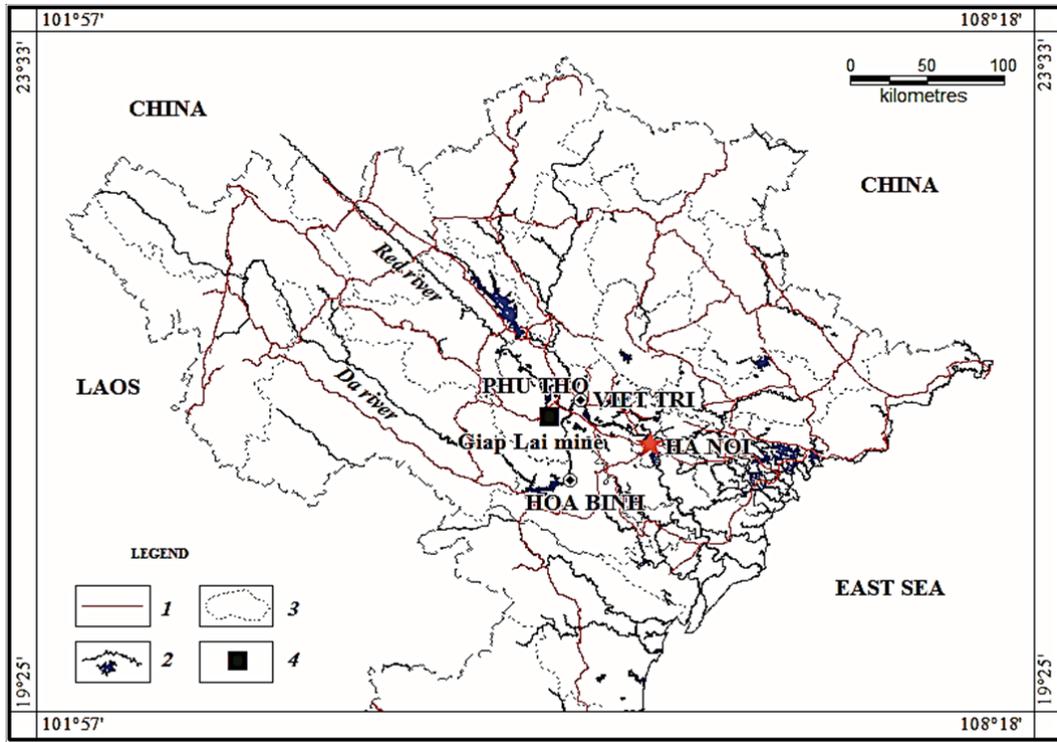
The vein type massive ore bodies were distributed in metamorphic rocks of the Thach Khoan formation (NP -  $E_1$  tk) consisting of two mica - garnet - quartz schist, mica - staurolite - disten schist, quartzite and marble.

The ore mineral compositions comprised mainly of pyrite ( $FeS_2$ ) with minor pyrrhotite ( $Fe(1-x)S$ ) and a very small amount of other sulfide minerals such as chalcopyrite ( $CuFeS_2$ ), galena (PbS), sphalerite (ZnS). The sulfur content (S) of ore ranges from 15 to 30% and average about 24.45% (Tran Xuan Toan, 1963).

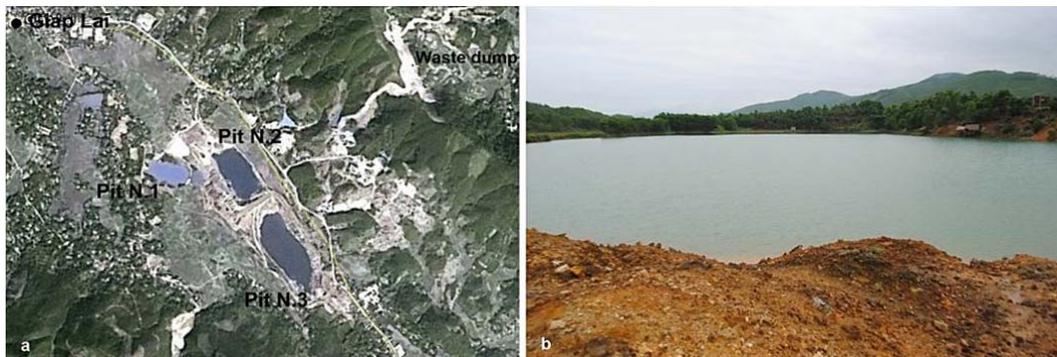
Mining of pyrite in Giap Lai mine occurred during the period 1975 - 1999, after which these operations ceased. The pyrite mine included 3 open pits which recently became 3 lakes (hereafter referred as lake No.1, No.2 and No.3) (Figure 2 and 3). During pyrite mining, a total of over 5 millions  $m^3$  of overburden was removed. Approximately, 1 million  $m^3$  of waste rocks were put into the waste dump, which located northeast of min-

ing pits, and a significant portion of rest waste rocks was used to backfill mining pits themselves. There are also 2 tailings deposits located in the north of mine (Figure 3). The first tailing dam was active until the late

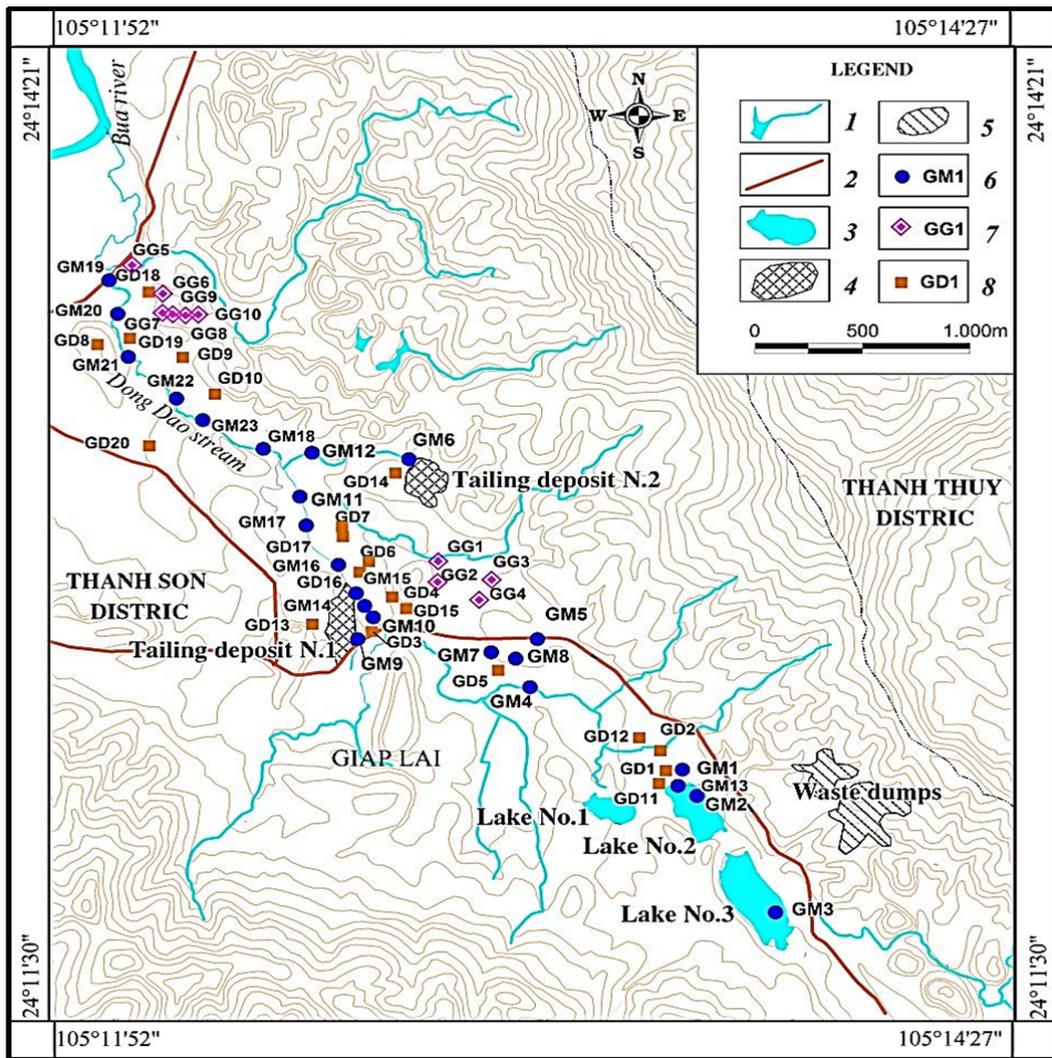
1980s and contains approximately 200,000 tons of tailings. The second dam operated from the late 1980s until mining ended and contains approximately 880,000 tons of tailings (Tarras-Wahlberg and Lan, 2008).



**Figure 1.** Map showing location of Giap Lai mine in Northern Vietnam  
1- Roads, 2- Rivers and Lakes, 3- Provincial boundaries, 4- Giap Lai mine



**Figure 2.** a) Three lakes are formed from old mining pits; b) view of Lake N.2 (open pit N.2)



**Figure 3.** Map of sampling sites at Giap Lai mining area  
 1- Water bodies, 2. Road, 3- Lakes (old pits), 4 - Tailing deposit, 5 - Waste dumps, 6 - Surface water sampling point,  
 7 - Ground water sampling point, 8 - Soil sampling points

### 3. Material and methods

The sample collection included 23 surface water samples (12 samples were taken during the rainy season and 11 others during the dry season), 15 samples of well water and 20 soil samples. Locations of sampling points are shown in Figure 3.

Each water sample was taken into 02 PE bottles of 0.5 L capacity and was treated with the ultrapure  $\text{HNO}_3$  solution to prevent precipitation. The water samples were filtered through a  $0,45\mu\text{m}$  filter paper.

The soil samples were taken in an amount of 1-2 kg from the surface layer (15 - 20 cm) and stored in PE plastic bags. In the laborato-

ry, samples were air-dried at room temperature. They were pulverized, then passed through 1 mm sieve to remove grit and plant residues. The fine fraction was well mixed, and about 100 g was removed using the quartered method, then was finally ground with an agate mortar.

The pH is measured by handheld pH meter HANA HI8424 with precision  $pH = \pm 0.01$ . Concentrations of Fe, Mn, Ni, Cu, Zn, Cd, Pb were analyzed by ICP-MS at the Institute of Geological Sciences, VAST, and concentrations of As, Se and Hg were analyzed by the same method using Vapor Generation Accessory (VGA-77).

Concentrations of Cu, Ni, Co in the leachates collected from experiments were analyzed by HACH DR2800 Spectrophotometer. The analytical precision for Co, Cu is  $\pm 0.01$  mg/L, and for Ni is  $\pm 0.001$  mg/L.

Experiments were carried out to evaluate the acid production potential and metal leaching of waste materials from tailings deposit No.1:

- Experiment No.1 was field test using paste-pH method (Sobek et al., 1978). The procedure is as follows:

The paste-pH test was performed in December 2015 (dry season). The samples for paste-pH test were taken in waste dump No.1 in a 1.5m deep profile. At each given depth in the profile a sample of ~ 100g (after removal of debris) was taken, and was mixed with deionized water at a ratio of 2:1 (solid: water), stirred, waited for about 30 minutes then measured for the pH.

- Experiment No.2 is leaching test performed in the laboratory using the modified procedure of AMIRA "Free Draining Leach Column Test" (AMIRA, 2002). The waste rocks from tailings deposit No.1 were taken for leaching experiment. The samples after removing soil and weathered, loosen parts were dried and crushed to 1-2 cm pieces. About 2 kg of chipped rocks were used for the experiment. The analytical columns were PET

5-liter vessels having a tap at the bottom for water draining. The experiment procedure is described as follows:

Step 1 (wet step): fill the column with 1.5L deionized water to submerge all of the test materials for 24 h.

Step 2 (humid step): after 24 h drain off water from the columns and leave still for 7 days (192 h).

After 7 days, repeat steps 1 and 2, this experiment was repeatedly performed over a period of 54 days (1344 hours).

At each draining, the leachates were measured for pH, Eh, Ec and analyzed for concentrations of some heavy metals using DR2800.

The impact magnitude is evaluated based on the comparison with the reference standards from Vietnam National Technical Regulations including QCVN03-MT 2015/BTNMT (on soil), QCVN08-MT 2015/BTNMT (on surface water), QCVN09-MT 2015/BTNMT (on ground water), QCVN01:2009/BYT (on drinking water) and QCVN02:2009/BYT (on domestic water).

Metal contamination of soil is also evaluated by Geoaccumulation index ( $I_{geo}$ ). Geoaccumulation index ( $I_{geo}$ ) was originally introduced by Müller (1969) and has been widely used since to assess contamination levels of heavy metals in sediments (Muler, 1969, Çevik et al., 2009, Ghrefat et al., 2011, Nowrouzi and Pourkhabbaz, 2015). The geoaccumulation index is also used to assess the contamination of soil (Loska et al., 2003; Wei et al., 2011; Zawadzki and Fabijan'czyk, 2013).

Geoaccumulation index  $I_{geo}$  is calculated using the below formula (after Muler, 1969; Loska et al., 2004):

$$I_{geo} = \log_2(C_n/1,5 \times B_n)$$

with  $C_n$  is the measured concentration of examined element  $n$  in the soil sample,  $B_n$  - reference value of the elements  $n$  and the factor 1.5 is used because of possible variations of the background data due to lithological variations. The quantity  $I_{geo}$  is calculated using the reference data of trace elements in soil from IAEA-soil-7 (IAEA, 2000).

Muller (1969) determined 7 classes from 0 to 6 according to  $I_{geo}$  values and 7 corresponding contamination levels, which are given in Table 1.

**Table 1.** Contamination categories based on geoaccumulation index ( $I_{geo}$ ) (Muller, 1969)

Class	Value	Classification
0	<0	Uncontaminated
1	0 - 1	Uncontaminated to moderately contaminated
2	1 - 2	Moderately contaminated
3	2 - 3	Moderately to strongly contaminated
4	3 - 4	Strongly contaminated
5	4 - 5	Strongly to extremely strongly contaminated
6	5 - 6	Extremely contaminated

## 4. Results

### 4.1. pH measurements

Table 2 presents the pH values in Pit (Lake) No.2 measured during the period 1995 - 2015. In 1997, when the mine was operational, thanked the applied control measures pH value of the water was normally high pH = 6.7. However, 3 years after mine closure, in 2002 the pH dropped to 3.1 (Table 2). Variation of pH values with time is shown in Figure 4. Surface water has pH ranged from 3.63 to 7.42, and 7 out of 23 samples have pH lower than the limit for irrigation water (QCVN08-MT 2015/BTNMT) and all of them are collected in the rainy season (Table 5). Water samples from wells have pH varying from 5.16 to 6.63 and generally meet the standard values for ground water (5.5 to 9 of QCVN09-

MT 2015/BTNMT), except for sample G15 having pH = 5.16, lower than the standard (Table 6).

**Table 2.** pH value of water in lake N.2 (old pit N.2) in time

	Time	Site	pH	Source
1	9/1997	Lake N. 2	6.7	1
2	5/2002	Lake N. 2	3.1	1
3	1/2011	Lake N. 2	5.2	2
4	3/2011	Lake N. 2	5.16	2
5	9/2011	Lake N. 2	4.8	2
6	6/2013	Lake N. 2	5.49	2
7	10/2015	Lake N. 2	5.35	2

Source: 1 - Håkan Tarras-Wahlberg, Lan T. Nguyen (2008); 2 - This study

### 4.2. Results of experiments

The paste-pH tests show low pH values at all depths of the profile (ranged from 3.66 to 3.88), indicating that the pore water is acidic (Table 3, Figure 5). The leachates in leaching experiments have low pH values (<2), while the concentrations of metals are very high. For example, concentrations of Cu, Ni and Co vary from 60 to 570 mg/L, 1.1 to 46.2 mg/l and 0.9 to 64.4 mg/l respectively. With time, pH values tend to increase, while the concentrations of metals decrease (Table 4, Figure 6).

**Table 3.** Results of paste-pH test in tailing N1

Sampes	Depth(cm)	pH	Sampes	Depth (cm)	pH
P-1	0 - 10	3.88	P-6	75 - 90	3.79
P-2	10 - 25	3.68	P-7	90 - 105	3.76
P-3	25 - 40	3.68	P-8	105 - 120	3.74
P-4	40 - 60	3.66	P-9	120 -135	3.76
P-5	60 - 75	3.71	P-10	135 -150	3.73

**Table 4.** pH and concentrations of some metals in leaching experiments

N.	Leachat	pH	T (°C)	Eh (mV)	EC (mS/cm)	Concentration (mg/l)			Time (h)
						Cu	Ni	Co	
0	0	7							0
1	TN1-01	1.77	30.9	260.2	130.2	570	46.2	59	24
2	TN1-02	1.72	30.5	266.7	123.9	232	20.6	64.4	192
3	TN1-03	1.77	30.8	268.2	90.3	104	4.8	14	384
4	TN1-04	1.86	28.4	254.3	67.1	78	2.8	7.4	576
5	TN1-05	1.82	29.8	258.4	62.5	70	2.2	4	960
6	TN1-06	1.85	30.7	264.5	56.6	64	1.5	2.8	1152
7	TN1-07	1.90	30.7	263.6	31.1	60	1.1	0.9	1344

Concentration of Fe, Cu, Ni, Co were analysed by DR2800 spectrophotometry in Department of Geochemistry, IGS - VAST

### 4.3. Heavy metal concentrations

Metal concentrations in the surface water vary in wide ranges (Table 5). Samples collected downstream of the lakes and the tailing impoundments shows high in Fe, Mn, Ni, Cu and As, but generally low in Pb, Cd, Hg and Se in all samples. In general, samples collected in the rainy season have higher metal concentrations as compared to samples collected in the dry season. Compared to the Standard (QCVN08-MT:2015/BTNMT, B1: irrigation water), in the rainy season, 10 out of 12 collected samples have Mn content exceeded the limit, but in the dry season, only one out of 11 analyzed samples have Mn content exceeded the limit. Similarly, for Fe, in the rainy season, 9 out of 12 samples have Fe content

higher than allowed level, but in the dry season, only one out of 11 samples have Fe content higher than allowed level. Some samples collected in the rainy season contain high Ni, while other samples, for example, sample M06 is contaminated by As (Table 5).

Heavy metal concentrations in the ground water are generally low, except for samples G3, G4 having high Mn (10.48 mg/L and 19.79 mg/L respectively) and Ni (0.065 mg/L and 0.52 mg/L respectively) and samples G13, G15 having high Mn contents (2.59 mg/L and 3.69 mg/L respectively) as compared to the standard for ground water (QCVN09-MT 2015/BTNMT). The heavy metal concentrations in other samples are met the standard norms (Table 6).

**Table 5.** pH and concentrations of some metals in surface water from Giap Lai mining area (mg/l)

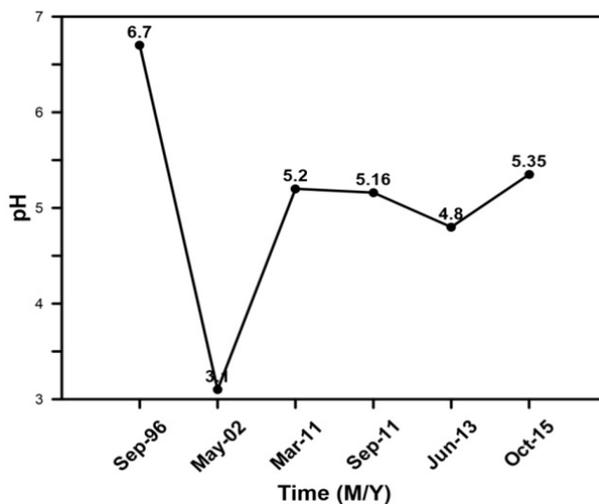
Samples	pH	Mn	Fe	Ni	Cu	Zn	As	Cd	Hg	Pb
M1	5.2	1.98	0.23	0.0178	0.0037	0.0345	0.00032	0.00032	0.0002	0.00399
M2	4.08	26.27	10.43	0.6441	0.1114	0.4642	0.00171	0.00406	0.0003	0.02774
M3	5.49	0.43	2.03	0.0104	0.0062	0.0439	0.00603	0.00024	0.0003	0.03223
M4	4.14	31.05	25.15	0.4448	0.0898	1.1375	0.00023	0.00571	0.0003	0.01112
M5	5.95	4.74	4.29	0.0641	0.0183	0.1864	0.00053	0.00087	0.0003	0.00361
M6	3.63	1.56	477.05	0.2013	0.3978	0.2441	0.99428	0.00105	0.0003	0.00400
M7	5.03	8.49	41.20	0.1024	0.0653	0.1574	0.00687	0.00149	0.0015	0.0594
M8	6.6	0.14	0.62	0.0042	0.0055	0.0226	0.00127	0.00003	0.0019	0.00176
M9	6.5	4.71	7.66	0.0641	0.0183	0.1833	0.00048	0.00084	0.0003	0.00357
M10	6.57	3.98	2.03	0.0384	0.0099	0.1601	0.00064	0.00005	0.0002	0.00249
M11	6.71	2.96	1.48	0.0269	0.0010	0.1391	0.00071	0.00004	0.0002	0.00287
M12	6.72	1.78	0.92	0.0178	0.0011	0.1058	0.00075	0.00003	0.0010	0.00301
M13	5.16	0.007	0.13	0.0259	0.0052	0.1473	0.00435	0.00052	0.0144	0.01506
M14	6.06	38.05	48.15	0.4448	0.0898	1.1375	0.00073	0.00571	0.00029	0.01112
M15	7.38	0.006	0.33	0.0010	0.0119	0.0094	0.00307	0.00005	0.00198	0.0008
M16	7.42	0.004	0.31	0.0010	0.0028	0.0156	0.00217	0.00004	0.00073	0.00085
M17	7.42	0.004	0.29	0.0011	0.0023	0.0161	0.00226	0.00002	0.00043	0.00081
M18	7.38	0.003	0.26	0.0009	0.0030	0.0101	0.00220	0.00003	0.00029	0.00054
M19	7.24	0.006	0.17	0.0007	0.0032	0.0139	0.00212	0.00004	0.00022	0.00054
M20	7.32	0.003	0.17	0.0009	0.0020	0.0114	0.00200	0.00003	0.00016	0.00032
M21	7.32	0.002	0.15	0.0008	0.0021	0.0107	0.00204	0.00003	0.00014	0.00030
M22	7.28	0.003	0.18	0.0008	0.0023	0.0084	0.00227	0.00002	0.00013	0.00044
M23	7.29	0.002	0.16	0.0007	0.0022	0.0098	0.00229	0.00003	0.00012	0.00034
Bua River	7.40			0.0004	0.0007	0.001	0.00024	0.00001	-	0.00012
STD	5.5-9	0.50	1.50	0.100	0.500	1.500	0.05	0.01000	0.0010	0.05

Note: M1 - M12: collected in the rainy season; M13 - M23: collected in the dry season. All samples were analyzed by ICP-MS in IGS - VAST. STD: Vietnam National Technical Regulations on surface water (QCVN08-MT:2015/BTNMT - B1: irrigation water)

**Table 6.** pH and concentrations of some metals in well water from Giap Lai mining area (mg/l)

Samples	pH	Mn	Fe	Ni	Cu	Zn	As	Se	Cd	Hg	Pb
G1	6.63	0.01	0.37	0.0080	0.0014	0.0156	0.0007	0.0007	0.0001	0.0017	0.0012
G2	6.53	0.15	0.36	0.0057	0.0031	0.0336	0.0012	0.0012	0.0001	0.0010	0.0010
G3	5.78	10.48	0.64	0.0646	0.0149	0.2159	0.0014	0.0009	0.0021	0.0008	0.0043
G4	5.83	19.79	1.45	0.5149	0.0348	0.3456	0.0007	0.0044	0.0048	0.0006	0.0018
G5	6.29	0.09	0.14	0.0039	0.0018	0.0242	0.0000	0.0002	0.0001	0.0009	0.0004
G6	5.8	0.64	0.10	0.0120	0.0016	0.0203	0.0006	0.0002	0.0003	0.0009	0.0009
G7	5.57	0.04	0.14	0.0029	0.1545	0.0268	0.0005	0.0017	0.0001	0.0007	0.0051
G8	5.9	0.21	0.11	0.0062	0.0014	0.1784	0.0001	0.0005	0.0002	0.0008	0.0004
G9	5.88	0.02	0.22	0.0013	0.0021	0.0217	0.0000	0.0012	0.0001	0.0004	0.0005
G10	5.66	0.09	0.07	0.0128	0.0039	0.0750	0.0025	0.0000	0.0001	0.0006	0.0005
G11	5.75	0.01	0.05	0.0010	0.0010	0.0228	0.0005	0.0003	0.0001	0.0004	0.0003
G12	6.56	0.00	0.12	0.0029	0.0014	0.0141	0.0002	0.0001	0.0000	0.0004	0.0005
G13	5.65	2.59	0.09	0.0173	0.0041	0.7456	0.0003	0.0006	0.0009	0.0005	0.0010
G14	6.2	0.96	0.52	0.0094	0.0029	0.0358	0.0069	0.0027	0.0004	0.0003	0.0003
G15	5.16	3.69	0.40	0.0321	0.0064	0.1002	0.0018	0.0059	0.0006	0.0003	0.0073
STD1	5.5-8.5	0.5	5	0.02	1	3	0.05	0.01	0.005	0.001	0.01
STD2		0.5					0.05				
STD3	6,5-8.5	0.3	0.3	0.02	1	3	0.01	0.01	0.003	0.001	0.01

Note: STD1: Vietnam National Technical Regulations on ground water (QCVN09-MT 2015/BTNMT); STD2 - Vietnam National Technical Regulations on domestic water (QCVN02:2009/BYT); SdT3: Vietnam National Technical Regulations on drinking water (QCVN01:2009/BYT)



**Figure 4.** Variation of pH in Lake N.2 (old pit N.2) with time

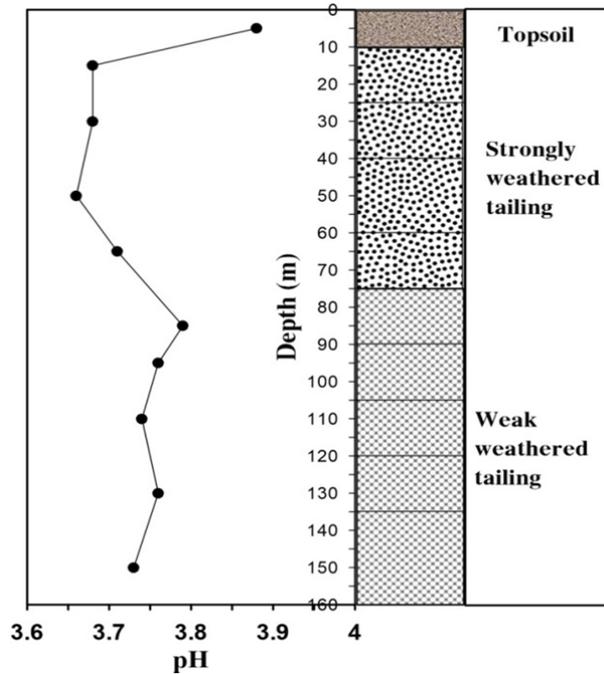


Figure 5. Variation of pH of waste material with depth in tailing N.1

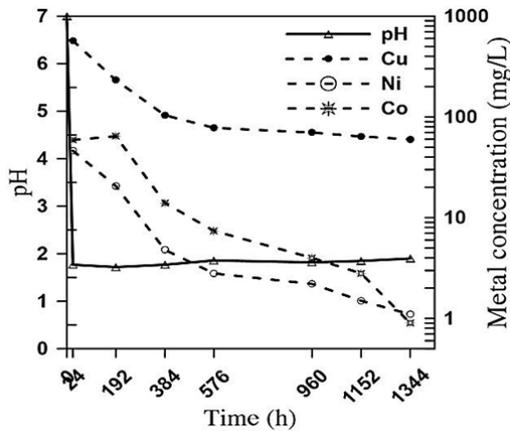


Figure 6. Variations of pH and concentrations of some metals with time in leaching experiments

Heavy metal concentrations of soil are shown in Table 7. Fe and Mn have relatively high contents ranging from 40936.3 mg/kg (dry weight) to 157147.6 mg/kg and 41.23 mg/kg to 3309.29 mg/kg respectively. Concentrations of As vary from 6.34 mg/kg to 370.63 mg/kg and 11 out of 20 analysed samples

have As contents exceeded standard for agricultural soil (QCVN03-MT:2015/BTNMT). Concentrations of Zn range from 56.89 mg/kg to 420.61 mg/kg and 4 out of 20 collected samples have Zn contents exceeded standard. Other metals such as Ni, Cd, Hg, Pb have low concentrations (Table 7), except for two samples D11 and D14 have high Pb contents (146.92 mg/kg and 142.64 mg/kg respectively), doubly exceeding the standard values.

## 5. Discussion

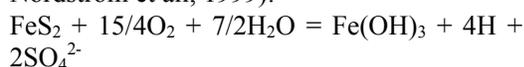
### 5.1. Acid rock drainage

Although Giap Lai pyrite mine has been closed for more than 10 years, the formation of acid rock drainage can be still observed in old pits and at many other places. Thus, 16 years after the mine closure acid drainage continues to occur in the old pits with low pH (Table 2 and Figure 4). Leakage appearing at the foot of the waste dumps and the tailing ponds is usually red in color and has very low pH, especially in the rainy season (e.g., sam-

ple M6 with pH at 3.63, Table 5). In the nearby rice paddies, where the acid leakage flows into, the rice withers in large strips (Figure 7).

As mentioned above, acid mine drainage or acid rock drainage formed by oxidation of sulfides, especially pyrite, which is the main mineral of the ore of Giap Lai mine, appears as the main cause of heavy metal pollution. High abundances of pyrite are still found in the old pits, waste dumps, tailings and former ore yards many years after the mine closure. The high concentration of pyrite under hot and high humidity tropical climate are viewed as ideal conditions for the acid rock drainage and heavy metal accumulation to form and disperse to the environment. As mentioned above, the sulfide minerals, especially pyrite, at surface condition can be easily oxidized to form sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). A summary equa-

tion for this process is as follows (after Nordstrom et al, 1999):



Surface water receives acid drainage and is directly affected, therefore many samples of surface water have lower pH values than a national standard (e.g., QCVN08-MT:2015/BTNMT, B1: irrigation water). The pH values of water in Dong Dao stream from watershed after Lake No.2 to the confluent with the Bua River vary from 4.14 to 7.42. In the upstream part where stream water directly receives acid drainage, the pH values are mostly low, but toward the downstream, the pH is rising because the stream water is diluted by other water sources unaffected by the ARD (Figure 8).

**Table 7.** Concentrations of some metals in soil from Giap Lai mining area (mg/kg)

Sampes	Mn	Fe	Ni	Cu	Zn	As	Cd	Hg	Pb
D01	3046.17	141226.1	59.68	62.23	<b>327.56</b>	<b>370.59</b>	0.51	0.33	33.24
D02	247.32	130236.4	54.61	59.72	<b>321.41</b>	<b>362.48</b>	0.48	0.3	28.76
D03	47.82	157147.6	47.4	45.03	69.72	<b>58.61</b>	0.28	0.38	4.51
D04	41.23	139672.3	37.45	40.09	60.21	<b>50.36</b>	0.3	0.28	4.2
D05	43.15	147357.2	43.02	41.42	63.46	<b>38.73</b>	0.21	0.3	4.35
D06	45.64	134341.7	42.13	39.46	58.74	<b>16.16</b>	0.2	0.3	4.2
D07	42.17	128530.8	39.07	37.52	58.61	7.44	0.2	0.31	3.94
D08	51.43	78432.56	37.61	36.58	57.43	6.63	0.21	0.37	4.02
D09	49.89	68456.32	34.61	36.58	57.43	6.63	0.21	0.37	4.02
D10	47.76	65024.72	35.47	36.35	56.89	6.34	0.2	0.36	4.1
D11	3309.29	123610.9	94.67	86.16	<b>420.61</b>	<b>104.57</b>	0.75	0.37	<b>146.92</b>
D12	344.11	141126.5	59.71	62.24	<b>327.68</b>	<b>370.63</b>	0.5	0.33	33.22
D13	47.82	157147.6	47.4	45.03	69.72	<b>58.61</b>	0.28	0.38	4.51
D14	329.76	40936.3	48.47	65.65	68.06	6.34	0.23	0.34	<b>142.64</b>
D15	42.38	146461.4	32.54	43.27	59.67	<b>37.35</b>	0.21	0.32	4.41
D16	46.47	154326.1	45.13	41.3	62.43	<b>25.42</b>	0.25	0.34	4.05
D17	43.05	149425.7	42.01	40.58	64.52	11.03	0.24	0.33	4.36
D18	52.34	78432.6	36.24	37.52	58.61	7.44	0.2	0.36	3.94
D19	51.43	65024.7	34.61	36.58	57.43	6.63	0.21	0.37	4.02
D20	49.36	68463.2	35.47	36.35	56.89	6.34	0.2	0.36	4.1
<b>STD</b>				<b>100</b>	<b>200</b>	<b>15</b>	<b>1.5</b>		<b>70</b>

Note: D1 - D10: collected in rainy season; D11 - D20: collected in dry season; STD: Vietnam National Technical Regulations on agriculture soil (QCVN03-MT 2015/BTNMT)

Generally, at all the observed points, surface water in the rainy season usually has lower pH than in the dry season. This difference is explained by the mobility of acid formed by pyrite oxidation. In fact, the for-

mation of acid is still ongoing even during the dry season, which is proven by the paste-pH experiments described above. However, in the dry season, the generated acid mostly remains in the pore water, whereas in the rainy season

it is mobilized by precipitation to the surface flow, as a result, lowering the pH of surface water. This phenomenon has also been noted in many places (Pham Tich Xuan et al., 2011).

Notably, the samples contaminated with heavy metal with relatively low pH are found near waste dumps, tailing ponds or former

mining pits. Acid generation and metal leaching potential of waste materials of Giap Lai mine have been proven by the experiments described above (Table 2 and 3). The negative correlation between pH values and heavy metal concentrations in surface water is shown using the Ficklin diagram (Figure 9).



Figure 7. a, b: leakage from tailings and c: from former ore yards, d: the rice withers in large strips because of ARD. Low pH leakage is red in color

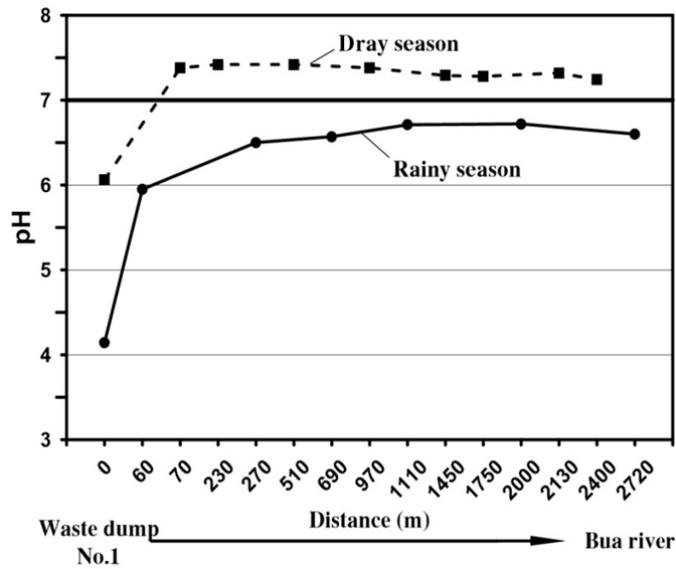


Figure 8. Graph showing the pH of Dong Dao stream from watershed to the Bua River

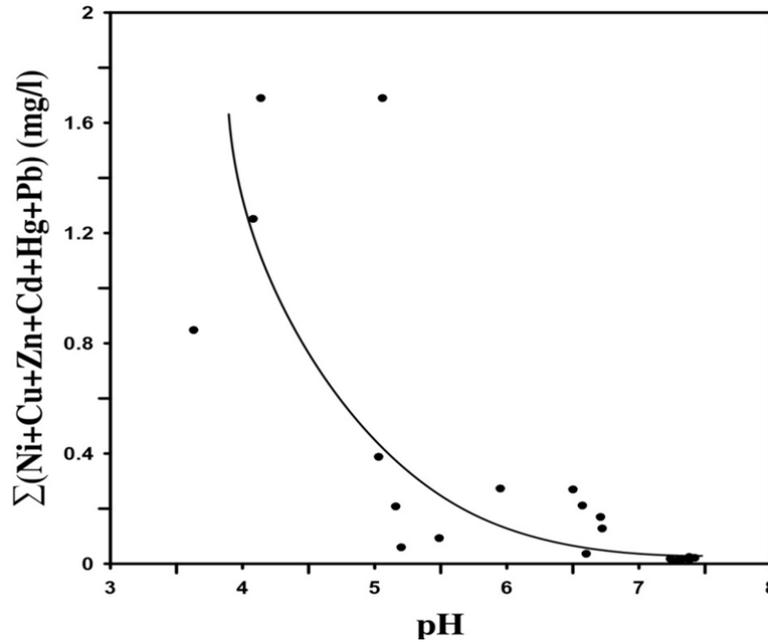


Figure 9. Ficklin diagram showing the correlation between pH and concentrations of heavy metals in surface water in Giap Lai mine area

5.2. Assessment of heavy metal pollution

5.2.1. Surface water

Except for Fe and Mn, which usually are very high in content, concentrations of other heavy metals in the majority of surface water samples at Giap Lai are relatively low, ranging from the acceptable levels (after

QCVN08:2015/BTNMT, indicators B1), but the serious impact of acid drainage on the surface water can be seen when compared with the acid-free water from Bua River. Concentrations of metals in surface water at Giap Lai mining area much higher than in Bua River water (Figure 10).

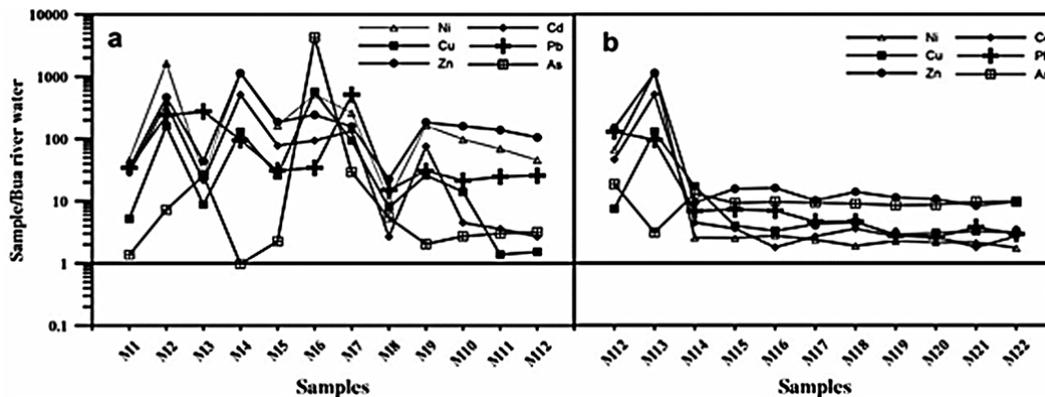


Figure 10. Concentrations of some metals in surface water in Giap Lai mine area normalized to those of Bua River water: a - rainy season, b- dry season

5.2.2. Ground water

The most of the samples of well water in Giap Lai mining area have relatively low metal concentrations ranging from the standard for groundwater. However, well waters in the Giap Lai mining area are directly used for drinking without treatment. Thus, compared to technical regulation on domestic water (QCVN02:2009/BYT), 11 out of 15 collected samples are not met the pH standard values. Moreover, comparing to drinking water standards (QCVN01:2009/BYT), the figure is much worse. Also, some samples show concentrations of Mn, Fe, and Ni exceeding the drinking water standards. In conclusion, quality of the groundwater and the water supply in the Giap Lai mine and surrounding area are problematic, needed to be taken care of.

5.2.3. Soil

Soil samples show pollution with As, Cu and Zn, especially heavy in the rainy season, when 11 out of 20 collected samples are polluted with As. Other metals such as Ni, Cd, Hg have low concentrations (Table 6). Notably, two samples D11 and D14 have high Pb contents, double exceeding the standard values. Most of the polluted soil samples are dis-

tributed near the old mining area and waste dumps.

Geo-accumulation index

The  $I_{geo}$  of soil samples from Giap Lai mine area are shown in Table 8. Ni has  $I_{geo}$  ranging from -0.26 to 1.28, classified as uncontaminated to moderately contaminated, while the average of  $I_{geo} = 0.22$  suggests the soil samples are uncontaminated to moderately contaminated. The  $I_{geo}$  of Cu ranges from 1.14 to 2.38 suggesting that the soil is moderate to strongly contaminated and the average of  $I_{geo} = 1.49$  indicates that the soil is moderately contaminated by this metal. Some samples have high  $I_{geo}$  values for As (up to 4.2), but the average  $I_{geo}$  for As = 1.96, indicating that the soil is moderately polluted by As. Hg has relatively high  $I_{geo}$  and the average of geo-accumulation index of Hg ( $I_{geo} = 2.5$ ) suggests that the soil is moderate to strongly contaminated by this metal. The  $I_{geo}$  of Zn, Cd, and Pb are low and the all of the averages of geoaccumulation index of these metals are negative suggesting that the soil is uncontaminated by these metals. The  $I_{geo}$  of soil samples from Giap Lai mining area show that soil in the study area is contaminated with Ni, Cu, As and Hg.

**Table 8.** Geoaccumulation indexes ( $I_{geo}$ ) of some metals in soil from Giap Lai mining ares (n = 20)

Metal	Concentration (mg/kg)				$B_n$ (IAEA-7)	Range of $I_{geo}$	$I_{geo}$ (Aveg.)
	$\bar{X}$	Min	Max	SD			
Ni	45.37	32.54	94.67	14.16	26.0	-0.26 ÷ 1.28	0.22
Cu	46.48	36.35	86.16	13.51	11.0	1.14 ÷ 2.38	1.49
Zn	118.85	56.89	420.61	119.80	104.0	-1.46 ÷ 1.43	-0.39
As	77.92	6.34	370.63	127.59	13.4	-1.66 ÷ 4.20	1.96
Cd	0.29	0.20	0.75	0.15	1.3	-3.29 ÷ -1.38	-2.73
Hg	0.34	0.28	0.38	0.03	0.04	2.22 ÷ 2.66	2.50
Pb	22.38	3.94	146.92	43.05	60.0	-4.51 ÷ 0.71	-2.01

6. Conclusions

Although Giap Lai pyrite mine has been closed down for many years the ARD still occurs and negatively impacts on quality of water and soil in the mining area.

Surface water in the mining area usually has relatively low pH (<5.5) and does not meet the Standard for irrigation water (QCVN08-MT:2015/BTNMT). The levels of Fe and Mn in surface water are very high, especially in the rainy season, in wich some

samples have Fe content up to 300 times, or/and Mn content up to 30 times higher than the Standards on irrigation water. Surface water shows slightly pollution of Ni and As, while other heavy metals such as Cu, Zn, Cd, Pb, Hg are lower than allowed limits. However, metal levels of surface water in mining area are much higher compared to the Bua River water, indicating metal contamination of surface water.

Generally, well water in Giap Lai mining area has pH and metal concentrations within the limit for groundwater (QCVN09-MT:2015/BTNMT). However, compared with standards for drinking and domestic water (QCVN01:2009/BYT and QCVN02:2009/BYT), the most of the well water have pH below the limit. Some samples show concentrations of Mn, Fe, and Ni exceeding the drinking water standards

Soil in mining area is polluted with Cu, Zn, Pb, especially in the rainy season. The geoaccumulation indexes show that soil in the study area is contaminated with Ni, Cu, As and Hg.

Pyrite-rich tailings and waste rocks are sources of ARD, causing elevated metal levels in downstream water bodies and soils, so samples located closely to these sources usually show contamination with metals.

Regardless of the fact that the mine is at an uncontrolled state after its closure with no post-closure remediation measures having been applied. The ARD originated from waste dumps and tailing ponds leaks out and flows into the nearby surface water bodies. Therefore, the risk of ARD and heavy metal contamination in this area remains high and will continue to affect the environmental quality. The research provides a series of evidence to suggest that the Environmental Protection Law should be fully implemented not only during mining but also after its closure.

#### Acknowledgements

This research work was financed by VAST Project (VAST05.05/15-16).

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