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Short Communication:

The Pattern of Heavy Metals Distribution in Time Chronosequence of Ex-Tin Mining Ponds in Bangka Regency, Indonesia

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Abstract: The heavy metals distribution of ex-tin mining ponds were investigated. The time chronosequence was determined at the pond of age < 1 year (Station A), the pond of age 5–10 years (Station B), and the pond of age > 15 years (Station C). The results showed sixteen heavy metals of As, Co, Cu, Cr, Fe, Ga, Hf, Ta, Te, Th, Mn, Ni, Pb, Zn, and V could be detected in the ponds. The metals such as As, Co, Cu, Mn, Ni, Pb, Th, and Zn in Station C showed higher concentration compared to the Station A and Station B. The metals such as Cr, Fe, Hf, Sn, Ta, Te, and V in Station A and Station B showed higher concentration compared to the Station C. The positive, negative, and dynamic correlation pattern could be found in distribution of heavy metal to time chronosequence. The concentration of Ta and V showed a positive correlation because their concentration decrease, whereas concentration of As, Cu, Ga, Mn, and Zn showed a negative correlation because their concentration increase along in time chronosequence. The dynamic correlation could be found that concentration of Co, Ni, Pb, Sn, and Th decrease from Station A to Station B and then increase in Station C, whereas concentration of Cr, Fe, Hf, and Te increase from Station A to Station B and then decrease in Station C.

Keywords: distribution pattern; heavy metals; chronosequence; ex-tin mining ponds

■ INTRODUCTION

Tin mining activity is an anthropogenic activity that has contributed to the ecological problems. It has been known as the major sources of heavy metal contamination such as heavy metals in ex-tin mining ponds. Ex-tin mining ponds as one of water resource were contaminated by heavy metals that can be accumulated in food chains 13 d secondary activities of the water [1-3]. Some of the heavy metals such as Pb, Zn, Mn, Fe, Cr, Cu, Ni, Sn, As, and Cd were detected in site of ex-tin mining [4-5].

The each of waters had their pattern of physical and chemical characteristics that determined by climatic, geomorphological, and geochemical conditions [6]. These conditions were influenced by ecological succession in time chronosequence [7] and the ecological changes of ex-tin mining ponds have occurred for a long time [8]. The implication of ecological changes as long as time chronosequence was interactions and reactions of chemical complexion between organic compounds, environmental sectors, and inorganic compounds, include presence of heavy metals [9].

The researches of heavy metals in ex-tin mining ecosystems have been done, however, not for correspondence of heavy metals distributions and ex-tin mining ponds in time chronosequence. While an understanding this correspondence was crucial to predict ecosystems conditions and to detect environment change. The understanding of heavy metals distribution in time chronosequence of ex-tin mining ponds becomes an important part of aquatic ecosystem management as water sources for secondary activities and habitable for organisms.

EXPERIMENTAL SECTION

Materials

The study areas were located in Bangka Regency, Bangka Belitung Archipelago Province of Indonesia. The considered study sites cover three ponds of ex-tin mining with chronosequence ranging in time. The study areas were encoded as Station A (pond in age < 1 year), Station B (pond in age 5–10 years), and Station C (pond in age > 15 years).

The coordinate of Station A were 01°59' S in points 36.0"; 36.2"; 36.4"; 36.5"; 36.6" and 106°06' E in points 36.5"; 36.9"; 37.3"; 37.4"; 37.5". The coordinate of Station B were 01°59' S in points 41.3"; 41.4"; 41.5"; 42.4"; 42.5" and 106°06' E in points 39.2"; 39.5"; 41.4"; 42.7"; 43.1". The coordinate of Station C were 01°55' S in points 40.9"; 58.9"; 59.1"; 59.2"; 59.5" and 106°06' E in points 19.5"; 19.7"; 19.9"; 22.4"; 29.2".

In the each of research stations points, water sampling was done < 4 m in depth (station code A.1; B.1; and C.1) and composite sampling were done to water and sediment > 4 m in depth (station code A.2; B.2; and C.2).

Instrumentation

The water samples and composite samples were analyzed pH value by pH meter (PH-009(I)-A) Sun Care. The speciation and concentration of heavy metals analyzed by X-Ray Fluorescence (Rigaku) with three light spreader metals of copper (Cu), molybdenum (Mo), and aluminum (Al). Also, the pH and moisture of soil around the ponds were measured by pH-moisture meter. The correspondence between heavy metals distribution and

the time chronosequence of ex-tin mining ponds was analyzed by PAST (*Palaentological Statistics*) 3.

RESULTS AND DISCUSSION

pH Value of Water and Soil

Tin mining activity had generated the ex-tin mining ponds as one of the water resources. However, water quality in the ponds had serious ecological problem. The ex-mining activity produced acid mine drainage (AMD) that can caused the long-term impairment of water quality and biodiversity. The pH value of ex-tin mining water and soil pH value indicated that the acid could be found in Station A (pond in age < 1 year) and Station B (pond in age 5–10 years) and the neutral value could be found in Station C (pond in age > 15 years). In the each of research stations points, water samples < 4m in depth indicated more acid than the composite samples (water and sediment > 4 m in depth) (Fig. 1).

The acid mine drainage (AMD) was produced when sulfide-bearing material is exposed to oxygen and gater [10]. In acid mine drainage, presence and mobility of elements such as Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn, and also ionic activity and sulphide

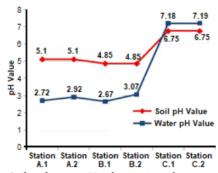


Fig 1. Soil and water pH value in time chronosequence of ex-tin mining ponds in Bangka Regency of Indonesia. The Station A (pond in age < 1 year), Station B (pond in age 5–10 years), and Station C (pond in age > 15 years). The station code (A.1, B.1, and C.1) showed water samples < 4 m in depth and the station code (A.2, B.2, and C.2) showed composite samples (water and sediment > 4 m in depth)

minerals oxidation caused pH value decreasing [11-12]. Furthermore, the low pH condition implicated in oxidation state, toxicity, and mobility of elements [9].

In long time chronosequence more than 15 years in the Station C caused changes water quality of ex-tin mining ponds were more stable than Station A and Station B. The indicator for it was pH value increased to neutral conditions (7.0-7.4) and other parameters that indicated water quality was more habitable for organisms' life such as fishes. The pH value and other parameters changes, indirectly, caused ecological productivity increasing. The chronosequence in long time caused changes in nutrient availability and resource supply for ecosystem productivity [13].

The pH value was found to play the most important role in the determination of metal speciation, solubility from mineral surfaces, movement, and bioavailability of metals. Furthermore, acid mine drainage had a major contribution in heavy metal contamination [14]. There was a negative correlation between soil pH and

distribution heavy metal where pH value decreasing caused increasing in heavy metal desorption [15].

The Pattern of Heavy Metals Distribution

The heavy metals that detected in ex-tin mining ponds were 16 element that As, Co, Cu, Cr, Fe, Ga, Hf, Sn, Ta, Te, Th, Mn, Ni, Pb, Zn, and V. All of these heavy metals were distributed in almost of research stations. Distribution of heavy metals can be grouped in low pH value or acid condition (in Station A and Station B) and neutral condition (in Station C) (Table 1).

There were nine heavy metals with higher concentration were found in Station C than Station A and Station B that As, Co, Cu, Ga, Mn, Ni, Pb, Th, and Zn. The average of As concentration were 1.7475 ppm (Station C) > 1.6075 ppm (Station B) > 1.0775 ppm (Station A). The concentration of Co were 3.32 ppm (Station C) > 2.525 ppm (Station A) > not detected (Station B). The concentration of Cu were 6.375 ppm (Station C) > 5.4825 ppm (Station B) > 4.9775 ppm (Station A).

Table 1. Distribution of heavy metals in time chronosequence in water of ex-tin mining ponds

							7.1	
	Heavy Metals	Heavy Metals Concentration (ppm)						
No		In Station A		In Station B		In Station C		
		Station A.1	Station A.2	Station B.1	Station B.2	Station C.1	Station C.2	
1	As	nd	2.155	nd	3.215	2.4	1.095	
2	Ga	12	4.275	nd	4.47	9.76	nd	
3	V	nd	0.84	nd	nd	nd	0.67	
4	Te	nd	nd	102	nd	nd	5.8	
5	Cr	nd	4.735	nd	4.945	nd	0.67	
6	Zn	nd	6.05	nd	8.1	8.17	3.905	
7	Sn	47	82.8	50.3	51.4	61.8	57.15	
8	Mn	nd	13.05	nd	13.6	30.8	14.85	
9	Fe	21.4	1481.3	148	2344	1590	849.05	
10	Co	nd	5.05	nd	nd	6.64	nd	
11	Ni	nd	4.09	nd	2.875	3.48	1.905	
12	Cu	3.08	6.875	3.19	7.775	8.94	3.81	
13	Pb	nd	6.7	nd	6	8.21	4.62	
14	Th	nd	4.605	nd	4.38	13.5	7.05	
15	Hf	6.71	3.21	8.21	3.32	nd	9.38	
16	Ta	4.94	2.615	4.16	2.995	nd	2.805	

^{*)} nd (not detected). The Station A (pond in age < 1 year), Station B (pond in age 5–10 years), and Station C (pond in age > 15 years). The station code (A.1, B.1, and C.1) showed water samples < 4 m in depth and the station code (A.2, B.2, and C.2) showed composite samples (water and sediment > 4 m in depth)

The concentration of Ga were 4.88 ppm (Station C) > 2.235 ppm (Station B) > 2.1375 ppm (Station A). The concentration of Mn were 22.825 ppm (Station C) > 6.8 ppm (Station B) > 6.525 ppm (Station A). The concentration of Ni were 2.6925 ppm (Station C) > 2.045 ppm (Station A) > 1.4375 ppm (Station B). The concentration of Pb were 6.415 ppm (Station C) > 3.35 ppm (Station A) > 3.0 ppm (Station B). The concentration of Th were 10.275 ppm (Station C) > 2.3025 ppm (Station A) > 2.19 ppm (Station B). The concentration of Zn were 6.0375 ppm (Station C) > 4.05 ppm (Station B) > 3.025 ppm (Station A).

In addition, there were seven heavy metals with higher concentration in Station A or Station B than Station C that Cr, Fe, Hf, Sn, Ta, Te, and V. The average of Cr concentration were 2.4725 ppm (Station B) > 2.3675 ppm (Station A) > 0.335 ppm (Station C). The concentration of Fe were 1246 ppm (Station B) > 1219.53 ppm (Station C) > 751.35 ppm (Station A). The concentration of Hf were 5.765 ppm (Station B) > 4.96 ppm

(Station A) > 4.69 ppm (Station C). The concentration of Sn were 64.9 ppm (Station A) > 59.475 ppm (Station C) > 50.85 ppm (Station B). The concentration of Ta were 3.7775 ppm (Station A) > 3.5775 ppm (Station B) > 1.4025 ppm (Station C). The concentration of Te were 51 ppm (Station B) > 2.9 ppm (Station C) > not detected (Station A). The concentration of V were 0.42 ppm (Station A) > 0.335 ppm (Station C) > not detected (Station B).

Their concentration of heavy metals in time chronosequence in ex-tin mining ponds showed three patterns distribution that a positive correlation, a negative correlation, and a dynamic correlation. The positive correlation indicated that concentration of heavy metals decreased along chronosequence in time in ex-tin mining ponds. The negative correlation indicated that concentration of heavy metals increased along chronosequence in time in ex-tin mining ponds. The dynamic correlation indicated that concentration of

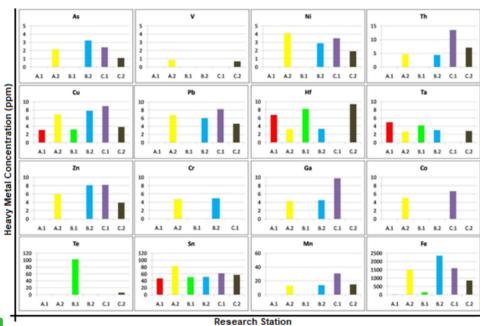


Fig 2. Distribution of heavy metals in time chronosequence of ex-tin mining ponds in Bangka Regency of Indonesia. The Station A (pond in age < 1 year), Station B (pond in age 5–10 years), and Station C (pond in age > 15 years). The station code (A.1, B.1, and C.1) showed water samples < 4 m in depth and the station code (A.2, B.2, and C.2) showed composite samples (water and sediment > 4 m in depth)

heavy metals on decreased or increased along chronosequence in time in ex-tin mining ponds.

The elements of Ta and V had a positive correlation in time chronosequence in ex-mining ponds with their concentration on decreasing. The elements of As, Cu, Ga, Mn, and Zn had a negative correlation with their concentration on increasing along time chronosequence. In addition, Co, Ni, Pb, Sn, and Th had decreased concentration from ponds with age < 1 year to ponds with age between 5-10 years and then increased concentration in ponds with age > 15 years. The elements of Cr, Fe, Hf, and Te had increased concentration from ponds with age < 1 year to ponds with age between 5-10 years and then decreased concentration in ponds with age > 15 years (Fig. 2).

The chronosequence in long time caused changes in heavy metals concentration were decreased as the primary succession progression [16]. The low pH value implicated to dissolved oxygen (DO) [17] and low DO in acid mine drainage implicated to biological oxygen demand (BOD) by microorganisms for their growth and other ecological factor changes such as nitrogen and phosphate [7,18-19]. Nitrogen (ammonia, nitrite, and nitrate) and phosphate were important for sustenance of various life forms,

primary succession, and led to changes in the biogeochemical cycles of nutrients in ponds [20-22], indirectly implicated to dissolved and suspended solid [23-24] and ecosystem eutrophic levels [25-31]. Therefore, pH value changes, availability of elements included heavy metals, environmental characteristics, and eutrophication had a positive inter-relationships in their correspondence.

These conditions, however, had a negative correlation to heavy metals residue decreasing in Station C. The heavy metals in Station C were dominated As, Zn, Mn, Co, Ni, Cu, Pb, and Th were higher than Station A and Station B, although these metals and include Ga, Cr, Sn, Fe, Hf, and Ta were detected in all of the research station. The results indicated that chronosequence in time of ponds caused ecological changes and had positive correlations, but not for distribution of heavy metals.

The Correspondence Analysis of Heavy Metals Distribution

The correspondence analysis also showed that there was not a positive correlation between in time chronosequence in water of ex-tin mining ponds and

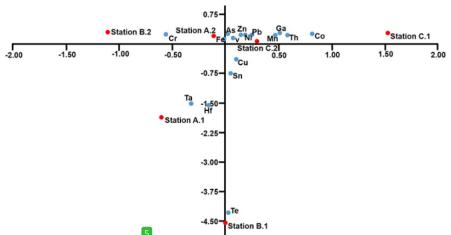


Fig 3. Correspondence analysis between distribution of heavy metals and in time chronosequence of ex-tin mining ponds in Bangka Regency of Indonesia. The Station A (pond in age < 1 year), Station B (pond in age 5–10 years), and Station C (pond in age > 15 years). The station code (A.1, B.1, and C.1) showed water samples < 4 m in depth and the station code (A.2, B.2, and C.2) showed composite samples (water and sediment > 4 m in depth)

heavy metals distribution (Fig. 3). The ecological changes in chronosequence succession of ex-tin mining ponds had not significantly affect on speciation and concentration of heavy metals. Thus, there was the other factor that had affected the distribution of heavy metals.

The soil and sediment of water contributed to the distribution of heavy metals [32]. In general, the mobility and availability of heavy metals were controlled by assorption and desorption characteristics of soils, include cation exchange capacity and the contents of clay minerals [15]. The clay and mud were found to be dominant in the sediment of Station A and Station B, however, sand was found to be dominant in Station C.

The clay and mud had a positive correlation and sand had a negative correlation to a presence, affinity and minerals structure [33-34]. The clay and mud had a larger surface area, higher cation exchange capability (CEC), and particles of clay in sediments were often closely associated with organic matter and also exist in the form of organic-mineral complexes. These particles adsorbed the active metals from the water phases, accumulated, and carried them to the bottom sediments diagenetically [35-36]. Therefore, distribution of heavy metals in Station A and Station B were lower than Station C.

CONCLUSION

In time chronosequence of ex-tin mining ponds had affected ecological dynamic such as pH value change and heavy metals distribution. The pH value of ex-tin mining ponds moved from acid to neutral condition, however, it had been taken for a long time of the chronosequence. The consequence of low pH value can implicated to microorganisms' growth, nutrients, and environment factors in primary succession. Further, it implicated to heavy metals interaction, whereas the heavy metals residue should be in low concentration in long time chronosequence of ex-tin mining ponds.

The heavy metals that detected in ex-tin mining ponds were 16 element that As, Co, Cu, Cr, Fe, Ga, Hf, Sn, Ta, Te, Th, Mn, Ni, Pb, Zn, and V. All of these heavy metals were distributed in almost of research stations. Distribution of heavy metals can be grouped in low pH value or acid condition (in Station A and Station B) and

neutral condition (in Station C). There were nine heavy metals with higher concentration were found in Station C than Station A and Station B that As, Co, Cu, Ga, Mn, Ni, Pb, Th, and Zn. In addition, there were seven heavy metals with higher concentration in Station A or Station B than Station C that Cr, Fe, Hf, Sn, Ta, Te, and V.

There were three patterns of heavy metals distribution in time chronosequence in ex-tin mining ponds that a positive correlation, a negative correlation, and a dynamic correlation. The chronosequence in time had affects on heavy metals distribution. Elements of Ta and V had a positive correlation in time chronosequence in ex-mining ponds with their concentration on decreasing. Elements of As, Cu, Ga, Mn, and Zn had a negative correlation with their concentration on increased along in time chronosequence. In addition, Co, Ni, Pb, Sn, and Th had decreased concentration from ponds with age < 1 year to ponds with age between 5-10 years and then increased concentration in ponds with age > 15 years. Elements of Cr, Fe, Hf, and Te had increased concentration from ponds with age < 1 year to ponds with age between 5-10 years and then decreased concentration in ponds with age > 15 years.

The chronosequence in time can be a factor that contributed to heavy metals distribution. However, the sediment factor had a significant effect to distribution of heavy metals in the ex-tin mining ponds, where clay and mud were more effective than sand in accumulation, adsorption, and interaction with heavy metals and carried them diagenetically to bottom sediments.

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