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PARIT NGAMARTO DRAINAGE EFFECTS ON BEKOK RIVER WATER QUALITY

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ABSTRACT

Bekok River is an important river which supply potable water for the community of Batu Pahat. The highly acidic and metal-polluted Bekok River is of major concern to the water treatment plant operations located at the downstream reach of the river. The problem is presumed to be the results of pyrite oxidation in acid sulfate soils, which occurs in the surrounding area of the river. Based on previous study, the construction of drainage system at Parit Ngamarto which part of Johor Barat Project was one of the possible cause of the presence of the pyrite oxidation. However there was yet no evidence to indicate the process. Hence, this study was initiated to study the occurrence of acid sulfate soil and soil oxidation process at Parit Ngamarto and its influence to Bekok River water quality. River and drainage water samples were collected and analysed for pH, SO_4^{2-}, electrical conductivity, Al, Fe and Mn concentrations. Soils sampled at various horizons were analysed for soil chemical characteristics. There was evidence that the deterioration of Bekok River water quality is probably due to the results of pyrite oxidation in the acid sulfate soils.

***KEYWORDS:* ACID SULFATE SOILS; PYRITE OXIDATION; WATER QUALITY.**

INTRODUCTION

The high acid level and metals concentration in a river system caused by drainage water from acid sulfate soils are of utmost concern if the river is to be used as a source of public water supply. Raw water with pH less than 3 would incur a tremendous treatment cost in terms of neutralizing agent (liming materials) before the water could be used by the public (WHO, 1985). Further reduction in pH value would cause the shutdown of the water treatment plant because the water may become toxic and unsuitable for drinking purposes (Ayob Katimon *et al.*, 2004). The high concentration of metals in public water supply could cause detrimental effects to human health.

Acid sulfate soils are naturally occurring soils containing iron sulfites (pyrite) or containing acidic products of the oxidation of the sulfite (Dent, 1986). These soils are characterized by low pH and high aluminium, iron and sulfate concentrations (Minh *et al*., 1997). Under waterlogged condition, the acid sulfate soil is stable and environment-friendly (Shamshuddin *et al*., 2004a). The improper use and management of acid sulfate soil could result in total degradation of water ecosystems by exporting toxic substances from soils to their adjacent water bodies (Lin *et al*., 1998). When it is disturbed, the acid sulfate soils are potent sources of acidity (Cook *et al.*, 2000) and metals contamination in surface water. Draining the acid sulfate soils to prevent water logging and drain surface runoff or for commercial or agricultural development will expose the pyrite to atmospheric conditions which will then be subsequently oxidized (Rassam *et al.*, 2002, Shamshuddin *et al.*, 2004b). The oxidation of pyrite also occurs following prolonged dry season and water table lowering (Auxtero *et al*., 1991, Nguyen and Wilander, 1995). During this period, these soils dry out and cracks form, which gives way for oxygen penetration to deeper layers resulting in oxidation of pyritic materials. The environmental hazards associated with acid sulfate soils arise mainly from the acids produced when pyrites are oxidized in the presence of water and oxygen. The oxygen is considered responsible for triggering the reaction since pyrites and water are readily available. The reaction of pyrite oxidation can be written as (Rassam *et al*., 2002)

$$4FeS_{2(s)} + 15O_{2(g)} + 14H_2O \rightarrow 4Fe(OH)_{3(s)} + 16H^{+}_{(aq)} + 8SO_4{}^{2-}_{(aq)} \quad \text{Eq. (1)}$$

Bekok River in recent years is facing severe water quality problem in term of pH. Between the months of January 2004 to May 2005, Bekok River registered a low pH of between pH 2.89 – 3.06. The latest monitoring programme conducted by Institute of Environmental and Water Resources Management (IPASA), between the months of February to May 2006 also confirmed the readings. Study by IPASA has identified severe acidic water (pH 2.6 to 3.8) contribution to Bekok river from most of its tributaries starting from Parit Ngamarto up to Bekok intake and Parit Ngamarto is an artificial constructed drainage This has caused operational problems to the water treatment plant that completely depending on the raw water supply from the Bekok River. The acidic water has caused corrosion of plant turbine and pipeline. Burst of pipe line has occasionally been reported resulting in water supply disturbance and shortages. The cost to neutralise the water has also increased and treatment scheduling became more complicated. The high level of acidity in the water has also resulted in higher metals content (Fe, Al and Mn) concentrations, which exceeded the allowable limit set by the National Standard for Drinking Water Quality. Thus, the study was carried out to gather information on *i*) the occurrence of acid sulfate soil in the surrounding area of the Bekok River *ii*) the properties of drainage channels water, and *iii*) water quality of Bekok River. The results showed that there was evidence to indicate the acidic and metal-polluted Bekok River is probably due to the results of pyrite oxidation in the acid sulfate soil.

MATERIALS AND METHODS

Soil sampling

The soils were sampled from two locations at Parit Ngamarto and Bekok River as shown in Figure 1. Soil sample were taken from five different depths (0-15 cm, 15-30 cm, 30-45cm, 45-60 cm and > 60 cm). Samples were immediately kept in plastic bags and tied tightly. The samples were then brought to the laboratory immediately. The pH of fresh soil samples was determined immediately at 1:1 soil- water ratio. The soil samples were air-dried, ground and sieved through a 2 mm sieve and determined for pH, exchangeable Al and Fe, water-soluble sulfate, electrical conductivity, total metals and water-soluble metals. The air-dried soil pH was determined in deionised water at soil to solution ratio of 1:1. The analysis of exchangeable Al and Fe were carried out by extraction using NH_4Cl (Shamshuddin *et al.*, 2004a) and determination by inductively coupled plasma-mass spectrometry (Elan 9000 Perkin Elmer ICP-MS). Water-soluble sulfate was extracted by shaking 10 g soil in 50 ml deionised water for 30 minutes followed by centrifugation at 2500 rpm. The extracted sulfate was determined by turbidimetric method. Electrical conductivity (EC) of the air-dried samples was measured in a suspension of soil in water at 1:5 ratios after 1 hour of intermittent shaking and overnight standing. Total metal analysis was carried out by dissolving appropriate amount of air-dried samples in aqua regia using microwave-assisted digestion method (Multiwave 3000 Anton Paar Microwave) and determined by ICP-MS. Water-soluble metals were extracted by shaking 10 g samples in 50 ml deionised water for 16 hours (Green, 2003) followed by centrifugation at 2500 rpm. ICP-MS was used to quantify the extracted water-soluble metals. Results obtained for exchangeable Al and Fe, total and water-soluble metals of Al, Fe and Mn and sulfate concentrations were calculated on dry weight basis.

Drainage channel water sampling

The drainage water samples were collected three times within five months between December 2007 and April 2008. Two litre water samples were collected at each sampling station. Drainage water samples from twenty identified drainage channels along the Parit Ngamarto as shown in Figure 1. The measurements of pH and electrical conductivity of the drainage water were made in the field using calibrated water quality checker Horiba U-22. Sulfate analyses for both samples were carried out by turbidimetric method using HACH DR 4001. 100 ml sub samples of each drainage water were filtered through a 0.45 µm membrane filter and acidified with HNO_3 to pH less than 2 prior to quantification by ICP-MS.

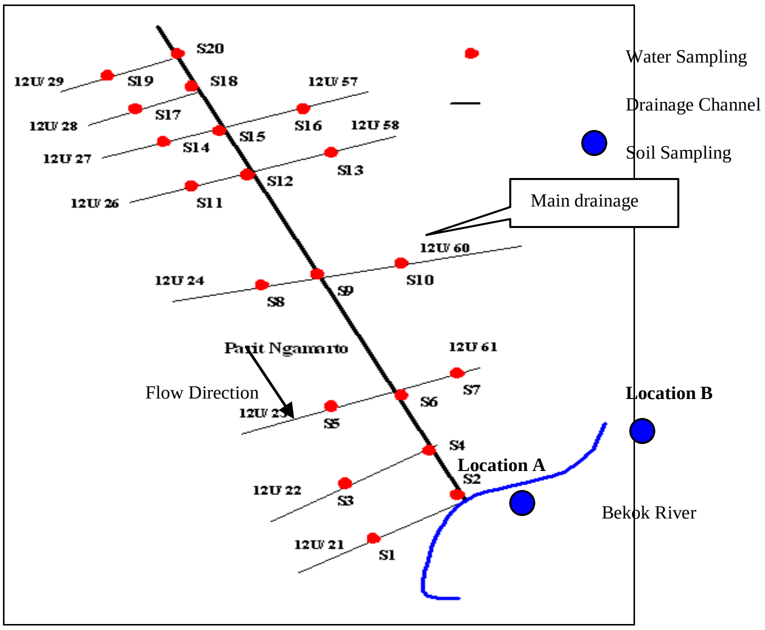


FIGURE 1: The map shows the water sampling stations, soil sampling and drainage channels locations along Parit Ngamarto.

RESULTS AND DISCUSSIONS

The chemical properties of the soil

Table 1 and Table 2 show the relevant chemical properties of the soils sampled from location A (Parit Ngamarto) and B (Bekok River). The fresh soil pH throughout the soil profile for both samples except the 45-60 cm and more than 60 cm depth of location A is less than 3.50. The pH became even lower after the soils were air-dried, presumably due to the oxidation of some pyrite still present in the soil (Shamshuddin *et al*., 2004a). The pyrite oxidation in acid sulfate soils produces high amounts of acidity resulting in further drop of pH value. The highest drop in soil pH after air-drying was in the > 60 cm depth at location A and in 15 – 30 cm depth at location B. The pH drop values were 1.18 and 0.17, respectively. This is consistent with the high amount of water-soluble sulfate in each soil depth with values of 3817.11 mg/kg and 1844.61 mg/kg, respectively. Sulfate is produced when pyrite undergoes oxidation when it is exposed to atmospheric conditions. These results are in agreement with the results obtained by Shamshuddin *et al.* (2004a). The amount of exchangeable Al throughout the soil profile is very high for both locations A and B. The values ranged from 9.48 cmol$_c$/kg to 14.01 cmol$_c$/kg for location A and 9.79 cmol$_c$/kg to 12.74 cmol$_c$/kg for location B. These high values are typical of acid sulfate soils in Malaysia (Shamshuddin *et al*., 2004a). The amounts of exchangeable Fe were also high, especially in the > 60 cm depth for location A and in the 45-60 cm depth for location B with values of 5.75 cmol$_c$/kg and 4.42 cmol$_c$/kg, respectively. The results obtained indicated the occurrence of acid sulfate soils in the surrounding areas of Bekok River watershed. Upon exposure to atmosphere, the pyrite in acid sulfate soils is oxidized, producing high amounts of acid and sulfate in soils. These are shown by the reduction of pH value and high concentration of sulfate in air-dried soil. High amounts of acid released attack the clay mineral liberating Al, Fe and other metals into soil. These can be shown by the results of high amounts of exchangeable Al and Fe in soils.

TABLE 1: Soil pH, exchangeable aluminium, conductivity and water-soluble sulfate in soil Location A

Depth	pH (fresh) (1:1)	pH (dry) (1:1)	pH drop value	Exchangeable cation, cmol$_c$/kg		Conductivity, µS/cm	Water-soluble sulfate, mg/kg
				Al	Fe		
0-15 cm	2.97	2.82	0.15	10.23	4.78	2550	2210.69
15-30 cm	2.95	2.83	0.12	12.59	4.89	1737	2701.46
30-45 cm	3.52	3.14	0.38	9.48	2.37	1264	2760.43
45-60 cm	3.85	3.11	0.74	14.01	5.51	1827	3202.41
> 60 cm	4.28	3.10	1.18	12.81	5.75	1696	3817.11

TABLE 2: Soil pH, exchangeable aluminium, conductivity and water-soluble sulfate in soil Location B

Depth	pH (fresh) (1:1)	pH (dry) (1:1)	pH drop value	Exchangeable cation, cmol$_c$/kg		Conductivity, µS/cm	Water-soluble sulfate, mg/kg
				Al	Fe		
0-15 cm	3.12	3.04	0.08	11.84	2.63	842	952.04
15-30 cm	2.95	2.78	0.17	9.79	2.47	1287	1844.61
30-45 cm	3.17	3.11	0.06	12.74	2.87	897	1106.60
45-60 cm	3.38	3.24	0.14	12.42	4.42	745	1062.28
> 60 cm	3.35	3.26	0.09	10.68	2.18	825	1297.27

The total metals and water-soluble metals in soil

Total metal analysis was carried out to determine the total Al, Fe and Mn in soils sampled at location A and location B while the water-soluble metal analysis were conducted to determine the amounts of water-soluble Al, Fe and Mn in soils which might have been released through pyrite oxidation. Total Fe in all soil profiles were high for both samples of location A and B with values ranging from approximately 142 000 µg/g to 244 000 µg/g and 111 000 µg/g to 322 000 µg/g, respectively as shown in Table 3. Total Al for soil samples of location A was high compared to total Al for soil samples of location B with values of 257 000 µg/g and 56 000 µg/g being the highest at each location respectively. Total Mn in all soil profiles were also high ranging from 1500 µg/g to 4700 µg/g for location A and 350 µg/g to 1300 µg/g for location B. Total Fe, Al and Mn obtained in this study were higher than the results obtained in the total metals analysis of acid sulfate soil at Kuala Linggi done by Shamshuddin (2004b). High amounts of Al were present in water-soluble form for both soils at location A and B with the highest value of 425 µg/g and 354 µg/g, respectively. High amounts of water-soluble Fe were also present in location A and B. However, low amounts of water-soluble Mn were detected which is in proportion of the low total Mn in both soils. These results were comparable with other research work performed by Shamshuddin *et al*. (2004b). The oxidation of pyrite in acid sulfate soils would, therefore, result in the release of high amounts of these metals into the environment, particularly into the rivers.

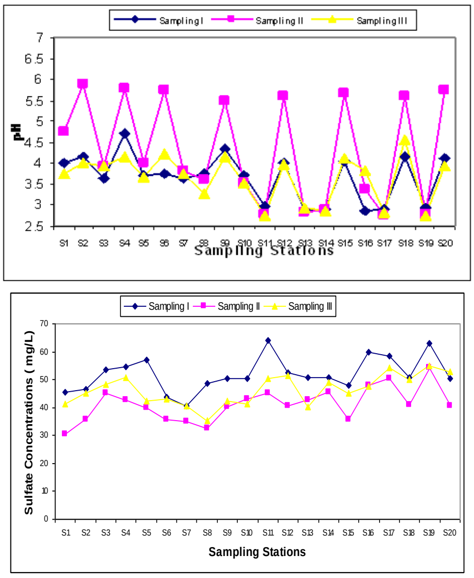
TABLE 3: Total metals and water-soluble metals of Al, Fe and Mn in soil for Location A and B

Depth, cm	Total Metals, µg/g						Water-soluble metals, µg/g					
	Location A			Location B			Location A			Location B		
	Al	Fe	Mn	Al	Fe	Mn	Al	Fe	Mn	Al	Fe	Mn
0-15	250798	210948	1564	48209	122528	397	200	127	6	76	135	3
15-30	211619	243803	4689	32552	322224	423	131	170	15	354	200	5
30-45	257315	141942	2466	54847	125181	1255	285	106	12	161	111	4
45-60	230566	168512	1511	55830	127247	582	309	106	15	121	117	3
> 60	235096	158971	1958	50008	110535	346	425	122	13	130	73	1

Drainnage Channel water quality

pH, and Sulfate

Figures 2 show the level of pH and sulfate concentration along the 10 km stretch of the drainage channel at Parit Ngamarto. The pH values for all measurements were in range 2.80 to 5.80. From Figure 2 (a), it was observed that the pH values increased as the drainage flowed downstream. The pH for main drainage are high between 3.77 to 5.90 but all the pH values for all measurement for tributaries for main drainage are lower than 3.94. It shows that the water in drainage channel are very acidic. It was also observed that during the high flow (sampling I), the pH values were lower than that of during the low flow (sampling II) and for sampling III, pH are average. This is in agreement with the finding of other study done by Ayob *et al.*(2004). It was probably because during rainy days, the leaching process was likely to happen more rapidly. Thus, a larger amount of soluble hydrogen ion would transfer through subsurface drainage from the soil profile into the drainage channels and subsequently into the river system. The high concentrations of sulfate were observed during the high flow compared to that of the low flow as shown in Figure 2 (b). The concentrations of sulfate during the high and low flow ranged from 40.5 mg/L to 64.2 mg/L and 30.5 mg/L to 54.4 mg/L, respectively. The reason can be explained in the same way as those of pH. The leaching of sulfate ion was likely to happen more rapidly during the high flow.

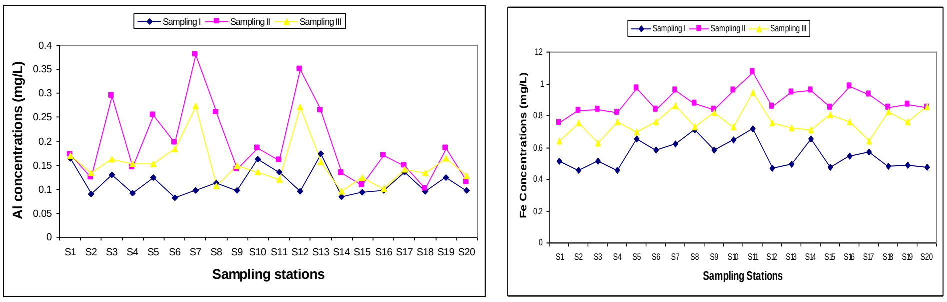


(a) (b)

FIGURE 2: Concentrations of (a) pH and (b) sulfate in Parit Ngamarto for various sampling stations

Al, Fe and Mn concentrations in drainage water

The profiles of Al concentrations at various sampling stations are depicted in Figure 3. The concentrations of Al from samplings were high, exceeding the acceptable limits of 0.2 mg/L for raw water supply. High concentrations of Al ranging from 0.102 mg/L to 0.38 mg/L in the river water samples were detected from the samples collected during the low flow condition. This might be due to the fact that the river water had already contained high amounts of Al before the first water sampling during the low flow condition was carried out. The same phenomenon may be used to explain the concentrations of Fe and Mn as shown in Figure 3 (d) and Figure 4. The high concentrations of Fe and Mn were also observed during the low flow condition ranging from 0.83 mg/L to 1.072 mg/L and 0.175 mg/L and 0.095 mg/L respectively. These values exceeded the limits of 1.0 mg/L for Fe but Mn are required in range 0.2 mg/L for raw water supply. The Al, Fe and Mn concentrations in water samples collected during the high flow condition were lower compared to that of during the low flow. This might be due to the amount of rainfall received within the periods, which had successfully flushed out those metals content from the river. These results were in agreement to the findings by Ayob *et al*. (2004). The dissolved Fe concentration was low during the period of rainy days.



(c)

(d)

FIGURE 3: Concentrations of (c) Al and (d) Fe in Parit Ngamarto for various sampling stations

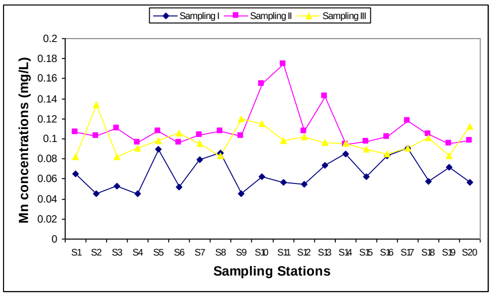


FIGURE 4: Concentrations of Mn in Parit Ngamarto for various sampling stations

CONCLUSION

This study has revealed that the pollution of low pH and high amounts of Al, Fe and Mn in Bekok River is probably due to the oxidation of pyrite in the acid sulfate soils occurring in the surrounding area of the river and Parit Ngamarto. This is indicated by low soil pH, high exchangeable Al and sulfate concentration detected in both soil samples from the two locations at Bekok River and Parit Ngamarto. Low soil pH and high exchangeable Al and sulfate concentrations were synonymous to the pyrite oxidation process. High amounts of water-soluble metals of Al, Fe and Mn were also the evidence of the occurrence of pyrite oxidation. The drainage channel water properties further indicated that the pyrite oxidation process occurred in the acid sulfate soil. Prolonged period of low rainfall in the area had resulted in the oxidation of pyrite in the soil. Intensive drainage and prolonged period of low rainfall had therefore led to the soil acidification resulting in highly acidic and metal-polluted Bekok River.

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REFERENCES

Ayob, K., K. Azrai, O. Fadil, S. Johan, Y. Zulkifli, H. Normala. 2004. Agriculture Drainage Affects River Water Quality. *The Institution of Engineers, Malaysia* 65 (1/2):1-7

Dent, D.L. 1986. Acid Sulfate Soil: A Baseline for Research and Development; International Institute for Land Reclamation and Improvement: Wageningen, The Netherlands, Publ. 39

Minh, L.Q., T.P. Tuong, M.E.F. van Mensvoort, J. Bouma. 1997. Contamination of surface water as effected by land use in acid sulfate soils in the Mekong River Delta, Vietnam. *Agriculture, Ecosystems and Environment* 61:19-27

Shamshuddin, J., S. Muhrizal, I. Fauziah, M.H.A. Husni. 2004a. Effects of adding organic materials to an acid sulfate soil on the growth of cocoa. *Science of the Total Environment* 323:33-45

Lin, C., M.D. Melville, M.M. Islam, B.P. Wilson, X. Yang, P. van Oploo. 1998. Chemical controls on acid discharges from acid sulfate soils under sugarcane cropping in an eastern Australian estuarine floodplain. *Environmental Pollution* 103:269-276

Rassam, D.W., F.J. Cook, E.A. Gardner. 2002. 1. Field and Laboratory Studies of Acid Sulfate Soils. *Journal of Irrigation and Drainage Engineering* pp 100-106

Shamshuddin, J., S. Muhrizal, I. Fauziah, E. Van Ranst. 2004b. A Laboratory Study of Pyrite Oxidation in Acid Sulfate Soils. *Communications in Soil Science and Plant Analysis* 35(1&2):117-129

Auxtero, E.A, J. Shamshuddin, S. Paramananthan. 1991. Mineralogy, Morphology and Classification of Acid Sulfate Soils in Pulau Lumut, Selangor. *Pertanika* 14(1):43-51

Nguyen, T.T. and A. Wilander. 1995. Chemical Conditions in Acidic Water in the Plain of Reeds, Viet Nam. *Water Research* 29(5):1401-1408

Green, C.H., D.M. Heil, G.E. Cardon, G.L. Butters, E.F. Kelly. 2003. Solubilization of Manganese and Trace Metals in Soils Affected by Acid Mine Runoff. *Journal Environmental Quality* 32:1323-1334