Dissolved and Suspended Particulate Metals in Setiu River Basin, Terengganu, Malaysia
(Logam Terlarut dan Partikulat Terampai di Lembangan Sungai Setiu, Terengganu, Malaysia)

M.K. KOH, S. SURATMAN & N. MOHD Tahir*

ABSTRACT
Dissolved and suspended particulate metals (Al, Fe, Cd, Cu, Zn, Pb) in Setiu River basin, Terengganu which is situated at coastal area of southern South China Sea were investigated. The water samples were collected from nine stations from June 2007 to January 2008, in conjunction with the Southwest monsoon and Northeast monsoon. The average concentrations of dissolved Al, Fe, Cd, Cu, Zn and Pb were (µg L\(^{-1}\)): 50±60, (2.0±3.4) ×10\(^2\), 2.5±2.6, 3.0±1.4, 7.5±5.1 and 6.0±5.0, respectively. Meanwhile, the concentrations of suspended particulate metals were (µg g\(^{-1}\)): (13±10)%, (10±13)%, 15±13, 65±94, (3.5±2.5) x10\(^2\), and (1.2±1.5) x10\(^2\), respectively. Seasonal variations of dissolved and suspended particulate metals were observed. The results were compared with selected Malaysian national rivers, world average and established guidelines. In addition, the enrichment of suspended particulate metals and the partitioning of metals between dissolved and suspended particulate phases were discussed.

Keywords: Dissolved and suspended particulate metal; enrichment factor; metal partition coefficient; Setiu River (Malaysia)

INTRODUCTION
Setiu River, with catchment area of approximately 188 km\(^2\) and 52 km in length, is located in Setiu district, east coast of Peninsular Malaysia. To date, Setiu is still a less developed district with low density of industrial activities. However, the 9-th Malaysia Plan has drafted the development of Setiu to become a portal of agricultural activities and ecotourism in the east coast of Malaysia (MDS 2009). Consequently, massive land clearing and construction activities to build infrastructure are being conducted at Setiu. The environmental stress is further exacerbated by the rapid population growth in Setiu district.

The Setiu River plays an essential role in the daily lives of local people as it supplies water for irrigation of agricultural land and support fresh water aquaculture. It also provides water for domestic usage, for which intake points are built along the riverbanks to extract raw water.

The Setiu River mouth is joined to a lagoon, well-known as Setiu Lagoon. Numerous studies have been conducted at Setiu Lagoon to monitor the water quality because of its economic contribution in supporting brackish water aquaculture and oyster farming (Suratman & Talib 2015; Suratman et al. 2014). Presently, it is observed that sand mining activities are actively operated along the river. Nevertheless, there has been a lack of study on the Setiu River quality despite the fact that Setiu River is discharging into the lagoon. In view of the fact that the degradation of Setiu River quality could impact the lagoonal system, a study on Setiu River basin is of utmost importance for better management of Setiu Lagoon. Considering the high dependence of local people on Setiu River and the gaps in knowledge, there is an apparent need to study the Setiu River quality.

Metal contaminations could have greater effect than organic or microbial contamination because metal...
could be cycled over a long time through aqueous and particulate phases (Manjunantha et al. 2001). Being aware of the potential threat of metals to the local human and ecosystem, the present study aimed to determine the dissolved and suspended particulate metals (Al, Fe, Cd, Cu, Zn, Pb) in Setiu River basin. The outcome of this study is likely to contribute to future research as the Setiu watershed is expected to become more complex and dynamic in terms of land use and population growth.

METHODS

Seven sampling trips to collect surface water samples at nine sampling stations, namely S1-S9 (Figure 1), were conducted between June 2007 and January 2008. The coordinate of the sampling stations are shown in Table 1. The study period coincided with Southwest monsoon (SWM) from June to September and Northeast monsoon (NEM) from late October to January.

The collected water samples were filtered through pre-weighed acetate cellulose membrane (with pore-size 0.45 μm) immediately after sampling. The filtrate were acidified with concentrated nitric acid to pH2 and kept frozen until analysis. The membrane filters were oven-dried and weighed to obtain the actual weight of suspended particulate matter. For determination of dissolved metals, thawed filtrates were directly injected into the inductively coupled plasma-optical emission spectrometer (ICP-OES). Extraction is not required since the salinity of water samples was lower than 0.5 ppt (Cenci & Martin 2004; Sturgeon et al. 1981). Closed digestions of the membrane filters were performed using aqua regia (mixture of concentrated HNO₃ and HCl at 1:3 ratio) in microwave oven at 180°C for 30 min. The resulted acid extracts were then analyzed with ICP-OES and the concentrations of suspended particulate metals were normalized to their dry solid weight. The analysis of dissolved and suspended particulate metals generally conforms to APHA-AWWA-WEF (2005) standard.

Other physical parameters such as pH, dissolved oxygen saturation (DO), temperature and salinity were measured in-situ using pre-calibrated YSI Multi-Parameter Water Quality Sonde. Monthly total rainfall of Setiu during the study period was obtained from Malaysia Meteorological Department (MMD). Essential quality control measures such as reagent blank analysis, standard addition and continuing calibration verification (CCV) were strictly practiced. All the blank controls gave insignificant levels of concentrations compared to samples.

![Figure 1. Location of Setiu district and sampling stations (S1-S9) distributed in Setiu River basin](image)

<table>
<thead>
<tr>
<th>Sampling stations</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Latitude</td>
</tr>
<tr>
<td>S1</td>
<td>5°35’40.80”N</td>
</tr>
<tr>
<td>S2</td>
<td>5°35’23.60”N</td>
</tr>
<tr>
<td>S3</td>
<td>5°32’48.73”N</td>
</tr>
<tr>
<td>S4</td>
<td>5°31’46.82”N</td>
</tr>
<tr>
<td>S5</td>
<td>5°29’48.60”N</td>
</tr>
<tr>
<td>S6</td>
<td>5°28’57.94”N</td>
</tr>
<tr>
<td>S7</td>
<td>5°36’37.16”N</td>
</tr>
<tr>
<td>S8</td>
<td>5°34’43.50”N</td>
</tr>
<tr>
<td>S9</td>
<td>5°33’22.07”N</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The percentage of recovery for standard addition and CCV were generally within the acceptable range (Table 2). Therefore, the employed analytical methods are suitable for metal determination.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Percentage of recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard addition (n=8)</td>
<td>CCV (n=15)</td>
</tr>
<tr>
<td>Al</td>
<td>89±6.0</td>
</tr>
<tr>
<td>Fe</td>
<td>71±14</td>
</tr>
<tr>
<td>Cd</td>
<td>97±0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>98±0.40</td>
</tr>
<tr>
<td>Zn</td>
<td>96±2.0</td>
</tr>
<tr>
<td>Pb</td>
<td>98±0.80</td>
</tr>
</tbody>
</table>

(note: mean±standard deviation)

PHYSICAL PARAMETERS

In-situ parameters such as pH, DO, temperature and salinity did not show significant variations between sampling trips and stations. The Setiu River is slightly acidic with average pH ranged from 5.80 to 6.30. Average DO levels were between 5.93 and 8.94 mg L⁻¹. The river water temperature was within 27.0 and 29.0°C. All the sampling stations are fresh-water dominated with salinity ranged between 0.01 and 0.03 ppt.

DISSOLVED METALS

Dissolved metals were measured in 63 samples and the results varied in a wide range between elements (Figure 2). Dissolved Al and Fe had much higher concentrations compared with other elements since they are Earth’s major elements. Strong correlation was found between dissolved Al and Fe ($r=0.75$, $p≤0.05$), suggesting that they could have similar origin. Seasonal variations were observed in the temporal distributions of dissolved Al.
and Fe, in which higher concentrations usually occurred during SWM compared to NEM. Therefore, the increases of rainfall during NEM appeared to have dilution effect on dissolved Al and Fe.

On the contrary, high rainfall during NEM increased the concentrations of dissolved Cd, Cu and Zn. Strong to moderate positive correlations were found between rainfall and dissolved Cd (r=0.88, p<0.01), Cu (r=0.60, p<0.20) as well as Zn (r=0.60, p<0.20), indicating that land surface runoff may contain considerable amount of these elements. The p-value of more than 0.05 could be ascribed to the insufficiency number of samples. Dissolved Cd was also strongly correlated with Cu (r=0.80, p<0.05). Unlike other elements, dissolved Pb had neither noticeable seasonal variations nor significant correlations with other dissolved elements.

Compared with selected Malaysian national rivers located within urbanized area such as Langat River, Juru River and Serin River, dissolved metal concentrations in Setiu River are generally lower (Table 3). Nevertheless, the concentrations of dissolved Cd, Cu and Pb were several folds higher than unpublished data acquired earlier by Noor Fazilah (2002), suggesting the increase of anthropogenic influences on Setiu watershed. In fact, the current results are higher than the world average for pristine river. To evaluate the Setiu River quality, concentrations of dissolved metals were assessed with drinking water guidelines proposed by World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) (Table 3). The assessment indicates that Setiu River is still complying with WHO and USEPA guidelines.

### SUSPENDED PARTICULATE METALS

The results infer that metals are predominantly in suspended particulate form compared with dissolved concentrations (Figure 3). Concentrations of suspended particulate Al and Fe were higher than other elements by 3–4 orders of magnitude. The suspended particulate metals exhibited clear seasonal variability, where higher and/or maximum concentrations generally occurred during NEM. This seasonal variation is more obvious in the temporal distributions of suspended particulate Fe, Cd, Zn and Pb. Increased of rainfall during NEM could have enhanced the input of metal-rich particulate materials into Setiu River. Strong inter-correlations were found between all the suspended particulate metals (0.70 ≤ r ≤ 0.99, 0.001 ≤ p ≤ 0.09), suggesting high probability of their common origin.

The concentrations of suspended particulate Al, Fe, Cd and Pb in Setiu River were higher than the world average while Cu and Zn are lower (Table 4). The results were also compared to Artois-Picardie Basin (APB) and SEQ-Eau scales for river suspended particulate metals classification (Table 4).

It should be noted that APB and SEQ-Eau scales were established for assessing the river suspended particulate metals pollution in France. Considering the climatic and geological differences between France and Malaysia, APB and SEQ-Eau scales may not classify the Setiu River quality accurately. However, the information from APB and SEQ-Eau scales are still adequate for reference while a Malaysian or international scale is yet to be established. In addition, theoretical values proposed in SEQ-Eau have not taken into account the natural background levels and hence it may overestimate the degree of pollution (Meybeck et al. 2007). With reference to APB scale, suspended particulate metals in Setiu River were still below the L₁ class, suggesting the absence of established contamination. Meanwhile, a more stringent assessment scale, SEQ-Eau, indicates that suspended particulate Cd and Pb were in the r-code, signifying the potential of extreme impact on ecology or human health.

To facilitate the estimation of metal enrichment in suspended particulate matter, Al-normalized enrichment factor (EF) was being calculated. The EF was expressed as the following equation (Gordeev et al. 2004):

### TABLE 3. Concentrations of dissolved metals in Setiu River, selected Malaysian national rivers and world average for pristine river. Drinking water guidelines proposed by WHO and USEPA

<table>
<thead>
<tr>
<th>Rivers</th>
<th>Average concentrations of dissolved metals (μg L⁻¹)</th>
<th>( \text{WHO}^{2} )</th>
<th>USEPA ( ^{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setiu</td>
<td>50±60 ((2.0±3.4)\times10^2)  \quad 2.5±2.6 \quad 3.0±1.4 \quad 7.5±5.1</td>
<td>2.0±10^2</td>
<td>3.0±10^3</td>
</tr>
<tr>
<td>Setiu</td>
<td>nd \quad 0.50 \quad 0.40 \quad nd</td>
<td>50±40</td>
<td>96±70</td>
</tr>
<tr>
<td>Neru</td>
<td>nd \quad 0.40 \quad nd \quad nd</td>
<td>50±40</td>
<td>96±70</td>
</tr>
<tr>
<td>Langat</td>
<td>60±3 ((6.0±2.0)\times10^2) \quad 1.4±0.60 \quad 5.2±4.9</td>
<td>6.0±20</td>
<td>9.0±40</td>
</tr>
<tr>
<td>Juru</td>
<td>nd \quad 50±100 \quad (1.5±4.0)\times10^2 \quad 25±80</td>
<td>1.0±100</td>
<td>3.0±10^3</td>
</tr>
<tr>
<td>Serin</td>
<td>nd \quad 5.0±4.0 \quad 40±50 \quad 96±70</td>
<td>50±70</td>
<td>50±70</td>
</tr>
<tr>
<td>World average</td>
<td>40 \quad 50 \quad 1.0\times10^{-3} \quad 1.4 \quad 0.20</td>
<td>4.0\times10^{-3}</td>
<td>4.0\times10^{-3}</td>
</tr>
</tbody>
</table>

\(*\text{nd**: not determine

(1) This study; (2) Noor Fazilah (2002); (3) Poh et al. (2004); (4) Yusof et al. (2009); (5) Abbas et al. (2008); (6) Ling et al. (2010); (7) Meybeck et al. (1996); (8) WHO (2008); (9) USEPA (2009)
### Table 4. Concentrations of suspended particulate metals in Setiu River and world average. Artois-Picardie Basin (APB) and SEQ-Eau scales for river suspended particulate metals classification

<table>
<thead>
<tr>
<th>Rivers</th>
<th>Average concentrations of suspended particulate metals (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al (%)</td>
</tr>
<tr>
<td>Setiu</td>
<td>13±10</td>
</tr>
<tr>
<td>World average</td>
<td>8.7±6.0</td>
</tr>
<tr>
<td>APB³,⁴</td>
<td></td>
</tr>
<tr>
<td>L₁</td>
<td>nd</td>
</tr>
<tr>
<td>L₂</td>
<td>nd</td>
</tr>
<tr>
<td>SEQ-Eau</td>
<td>g</td>
</tr>
<tr>
<td>r</td>
<td>nd</td>
</tr>
</tbody>
</table>

L₁: probable contamination level, L₂: established contamination, g: green with some contamination without ecological or human health impact, r: red with extreme impact

1) This study; 2) Viers et al. (2009); 3) Meybeck et al. (2007); 4) Lourino-Cabana et al. (2010)

\[
EF (X) = \frac{[X/Al]_{(\text{sample})}}{[X/Al]_{(\text{world average})}}
\]

The average metal concentrations in world rivers suspended particulate matter are adapted from Viers et al. (2009). EF of >1 indicates enrichment; <1 indicates depletion; =1 indicates no changes in the relative abundance of element. Compared with world average, Fe (1.20), Cd (6.30) and Zn (3.90) are enriched in Setiu River suspended particulate matter while Cu (0.57) and Pb (0.40) are in depletion. The parenthesis indicates EF of respective metals. Notable Cd and Zn enrichment could be attributed to localized input from domestic sewage and...
agro-based industries. Untreated domestic sewage could be discharged into Setiu River through point and/or non-point sources since there is a lack of sewage treatment facilities within the watershed. Fertilizer and herbicide application to arable land could also lead to Cd and Zn enrichment as these elements often exist as impurities (Gimeno-Garcia et al. 1996; Luo et al. 2007; Zhang & Shan 2008). Despite the anthropogenic source, contribution of local lithology (natural source) to Cd and Zn enrichment could not be ruled out. However, we are uncertain of the relative importance of anthropogenic versus natural sources of suspended particulate Cd and Zn due to the lack of published geochemical data for Setiu area.

METAL PARTITION COEFFICIENT

The metal partition coefficient ($K_p$) describes the ratio of suspended particulate metal concentration (normalized to dry solid weight) to dissolved metal concentration. $K_p$ is expressed as the following equation (Allison et al. 2005):

$$K_p = \frac{\text{Concentration of suspended particulate metal (µg g}^{-1})}{\text{Concentration of dissolved metal (µg L}^{-1})}.$$  

Linear isothermal expression of $K_p$ assumes local or instant equilibrium of particulate and dissolved metals (Gallo et al. 2006). $K_p$ computation is useful for quantifying the relative sorption strength of individual metal to particulate matter. The sorption strength of metals to particulate matter will determine their fate and transport in the aquatic environment (Benoit & Rozan 1999; Gueguen et al. 2011). In general, metals complexes with particulate matter are considered to be less bioavailable than ionic or dissolved metals. Average ($n=63$) $K_p$ for Al, Fe, Cd, Cu, Zn and Pb are (L$^{-1}$g): (6.80±9.40)$\times 10^3$, (1.40±2.00)$\times 10^3$, 25.0±85.0, 23.0±55.0, 70.0±150.0 and 80.0±230.0, respectively. Therefore, relative sorption strength of measured elements are in decreasing trend of Al>Fe>Pb>Zn>Cd>Cu. The $K_p$ for Al and Fe are higher than Pb, Zn, Cd and Cu by two orders of magnitude. This result infers that major elements (Al and Fe) have higher particle sorption affinity compared with trace elements (Pb, Zn, Cd and Cu). In nature, Al and Fe are considered as dominant sorbents because they are common in rivers and soils, where they tend to coat other particles (Gaillardet et al. 2005). Therefore, it could be deduce that a major fraction of Al and Fe are transported with solid phase. Meanwhile, trace metals (Pb, Zn, Cd and Cu) exist in relatively labile ionic form or dissolved form (Hamad et al. 2012). The observation on the distinctness of $K_p$ for major elements and trace elements was also reported by Benoit and Rozan (1999). The large standard deviation indicates

![FIGURE 4. Variations diagram of Log $K_p$ versus TSS concentrations for studied elements](image-url)
that $K_e$ has scatter distribution and hence the partition of metals in suspended particulate and dissolved form is considerably unstable. Forcing factors such as rainfall event, pollutant plume emission and river hydrodynamic could have resulted in the $K_e$ variations (Gueguen & Dominik 2003; Owen et al. 1996).

Variations diagram of Log $K_e$ for each elements were plotted using total suspended solid (TSS) concentrations as x-axis (Figure 4). The $K_e$ of all elements appears to have inverse correlation with TSS. This inverse correlation is frequently discussed in related literatures and is commonly termed as ‘particle concentration effect’ (Balls 1989; Jiann et al. 2005; Koshikawa et al. 2007). The inverse relationship usually occurs when substantial amount of free-metals bound to colloids which may not be retained in filtering processes due to their small particle size ($1.20 \mu m-1kDa$) (Gallo et al. 2006; Moran et al. 1996). The low salinity in our study area could have enhanced the suspension of metal bound colloids in water column. In high salinity condition, colloids are susceptible to coagulation and thereby forming larger settling particles (Gueguen & Dominik 2003).

CONCLUSION

Based on the study of dissolved and suspended particulate metals in Setiu River, the following conclusions can be drawn:

Average concentrations of dissolved Al, Fe, Cd, Cu, Zn and Pb are ($\mu g$ L$^{-1}$): $50\pm60$, $2.0\pm3.4 \times 10^2$, $2.5\pm2.6$, $3.0\pm1.4$, $7.5\pm5.1$ and $6.0\pm5.0$, respectively. Higher rainfall during NEM appeared to have dilution effect on dissolved Al and Fe while Cd, Cu and Zn were enriched. The concentrations of dissolved Cd, Cu and Pb were several folds higher than unpublished data acquired in year 2002. However, the Setiu River quality is still complying with WHO and USEPA guidelines.

Average concentrations of suspended particulate Al, Fe, Cd, Cu, Zn and Pb are ($\mu g$ g$^{-1}$): $(13\pm10)$%, $(10\pm13)$%, $15\pm13$, $65\pm94$, $(3.5\pm2.5) \times 10^2$ and $(1.2\pm1.5) \times 10^2$, respectively. Higher and/or maximum concentrations of suspended particulate metals generally occurred during NEM. The suspended particulate Al, Fe, Cd and Pb in Setiu River are higher than the world average concentrations while Cu and Zn are lower.

Relative sorption strength of metals to particulate matter are in the decreasing trend of Al>Fe>Pb>Zn>Cd>Cu. The $K_e$ of all elements shows inverse correlation with TSS, owing to the ‘particulate concentration effect’.

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M.K. Koh, S. Suratman & N. Mohd Tahir*
Institute of Oceanography & Environment
Universiti Malaysia Terengganu
21030 Kuala Terengganu, Terengganu Darul Iman
Malaysia

N. Mohd Tahir*
School of Marine Science and Environment
Universiti Malaysia Terengganu
21030 Kuala Terengganu, Terengganu Darul Iman
Malaysia

*Corresponding author; email: hayati@umt.edu.my

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