World Applied Sciences Journal 8 (4): 496-502, 2010
ISSN 1818-4952

Organic Matter, Nutrients and Trace Metals of Serin River

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Abstract: Animal and fish farming may lead to water quality deterioration. Water quality of the Serin River was assessed at seven selected stations over six sampling trips. The tributary with animal farm discharge had the lowest DO (2.2 mg/L), highest BOD_5, phosphorus (P), ammonia-nitrogen (TAN), organic-nitrogen (org-N), TKN and Cu and second highest in nitrate-nitrogen (NO_3-N) and Ni. The station with fish culture recorded the highest Ni, Cd and DO (5 mg/L) and third highest in Inorg-P, Org-P and Pb. Near the village and school, Cr was the highest and Org-P was second highest. Stations by the road and bridge recorded the highest zinc, lead and second highest in copper attributable to vehicles. Downstream of animal farm discharge with discarded e-waste, old tires and glass also recorded high Zn, Pb and Cd. The station near crop farming showed highest NO_3-N, second highest in BOD_5, Inorg-P, TAN and Ni and third in Cd and Cr attributable in inorganic fertilizers. Trace metals complied with the USA drinking water criteria except Cd at the tributary receiving animal farm effluent and Pb at all stations. Principal component analysis showed classification of heavy metals according to sources. Effluent from animal and fish farms need to be treated, solid waste need to be recycled and stormwater need to be treated to protect the water quality of the river.

Key words: Agriculture · Nutrients · Trace metals · Serin River · Malaysia

INTRODUCTION

Serin River is located in the state of Sarawak, Malaysia. It supplies drinking water to the nearby residential and commercial areas. Therefore, it is necessary to ensure that the quality of the river water is suitable for such purpose. Human activities identified in the watershed include animal farming, agriculture and waste disposal. Animal farm effluent is an environmental concern as it contains high solids, organic matter, nitrogen (N) and phosphorus (P) which results in high biochemical oxygen demand (BOD) and low dissolved oxygen (DO) levels [1- 5]. Moreover, trace metals are often associated with animal farm effluent which may affect the water quality of the Serin River. Zn, which is often used as a feed additive in swine diets to control scours in pigs [6] and to improve feed efficiency; mostly ends up in the farm wastewater [3]. Pb and Ni concentrations in contrast were reported to be typically less than 5 mg/kg dm in compound and home-mix swine feeds as well as in pig manures [7]. One mineral supplement sample however was found to contain 12.9 mg/kg dm Pb while several slurry samples were found to contain more than 10 mg/kg dm Ni which are considered high concentrations [7].

Fish farming practices on the other hand often include the use of feed and fertilizers to promote fish production and usually only 25 - 30% of N and P in the feed and fertilizers are recovered in fish at harvest [8]. As such, fish pond effluents contain higher concentrations of nutrients, organic matter, suspended solids and plankton that may adversely affect the receiving water body when it is discharged during harvest [8, 9]. Crop production similarly poses an environmental concern as agricultural runoff is associated with increased P loading in receiving waters [10]. The elevated nutrient content can accelerate eutrophication in the stream which will potentially affect the Serin River in terms of decreased oxygen and water clarity, pH fluctuations and increased algae growth including toxin-releasing blue-green algae [11]. Due to the potential environmental concerns associated with the Serin River, this study aimed to assess its water quality.

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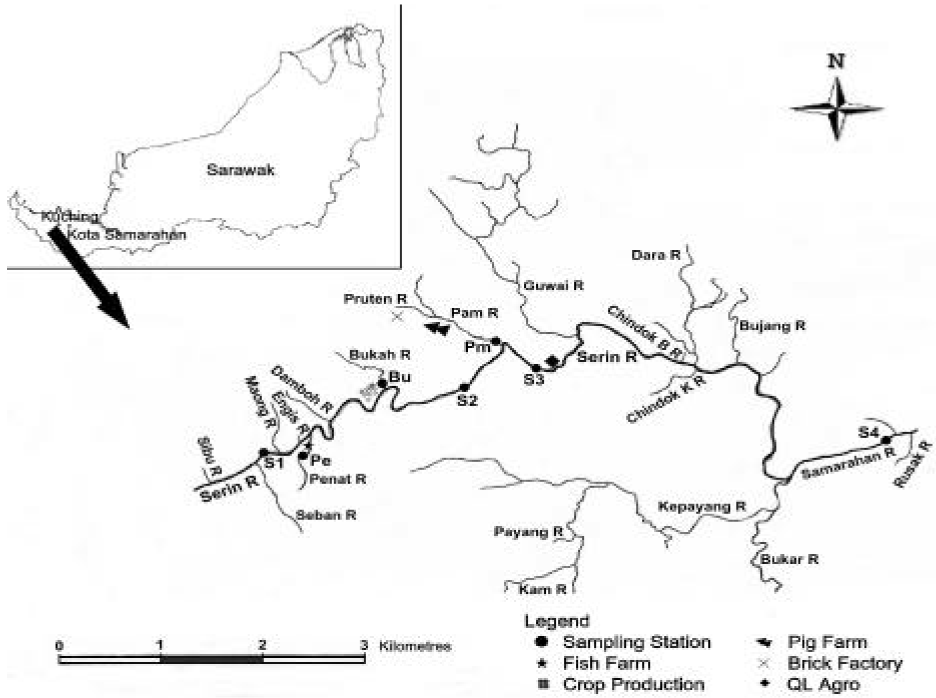

Fig. 1: The location of each sampling station and human activities in the watershed

MATERIALS AND METHODS

Study Site and Sampling: Seven stations on the Serin River were selected for this study as shown in Figure 1 where four stations were situated on the main river (S1, S2, S3 and S4) and three stations were located each on its tributaries, the Penat River (Pe), Bukah River (Bu) and Pam River (Pm). Six samplings trips were conducted between December 2008 and April 2009. Grab samples of river water were collected using 2L polyethylene bottles for nutrients analysis. Water samples for heavy metals analysis were collected in 1L polyethylene bottles and acidified immediately with concentrated nitric acid to pH less than 2. All samples were stored in a cooler box at 4°C before transport to the laboratory for analysis [12]. Temperature, pH and DO were measured in-situ with a multi-parameter water quality monitor (YSI 6600).

Laboratory Analysis: Parameters analyzed included biochemical oxygen demand (BOD_5), organic (Org-P) and inorganic (Inorg-P) phosphorus, total ammonia nitrogen (TAN), organic nitrogen (Org-N), total Kjeldahl nitrogen (TKN) and trace metals (Ni, Zn, Pb, Cd, Cr and Cu). BOD_5 analysis was performed according to [12]. Inorg-P was analyzed using the Ascorbic Acid method and the concentration determined with a spectrophotometer (Hach DR/2010) [13]. Org-P was calculated as the difference between total phosphorus (TP) and Inorg-P. For TP analysis, samples were digested concentrated nitric acid and concentrated sulfuric acid to oxidize organic matter and release organically-bound phosphorus as orthophosphates and the resulting concentration determined by ascorbic acid method [12; 13]. For nutrient analysis, TAN and NO_3^--N were analyzed according to Nessler method and cadmium reduction method [13] respectively while TKN was performed according to Standard Methods [12]. Then, concentration of Org-N was taken to be the difference between TKN and TAN. The water samples for heavy metal analysis were filtered before analysis using Inductive Coupled Plasma Mass Spectrometry (ICP-MS) (Shimadzu, ICPM-8500). The solution was analyzed for Ni, Zn, Pb, Cd, Cr and Cu. All samples were analyzed in triplicates.

Statistical Analysis: Data were analyzed using two-way ANOVA. Pairwise comparisons using Least Significant Difference procedure were also conducted to test for significant difference between all pairs of stations. Factor analysis using principal component analysis as the extraction method was conducted on heavy metals data to determine the sources of variation. All statistical analysis was conducted using SPSS version 16.

RESULTS AND DISCUSSION

The mean temperature, pH, DO, BOD_5, Org-P and Inorg-P values are summarized in Table 1. Temperature ranged from 23.53 at S1 to 25.36°C at S4. However, analysis indicated that there was no significant difference among the stations ($P = 0.326$). The pH values ranged

Table 1 Mean values of temperature, pH, DO, BOD_5, Org-P and Inorg-P of seven sampling stations

Stations	Temperature (°C)	pH	DO (mg/L)	BOD_5 (mg/L)	Org-P (mg/L)	Inorg-P (mg/L)
S1	23.53 ± 3.07^a	6.84 ± 0.68^{ab}	3.67 ± 1.91^{ab}	2.05 ± 0.17^a	1.41 ± 1.47^a	0.21 ± 0.36^a
S2	25.26 ± 1.58^a	7.44 ± 0.39^a	3.35 ± 0.90^{ab}	1.86 ± 0.39^a	0.45 ± 0.72^a	0.04 ± 0.04^a
S3	25.30 ± 1.65^a	7.33 ± 0.27^a	4.36 ± 1.69^a	2.65 ± 0.79^a	0.81 ± 0.95^a	0.10 ± 0.11^a
S4	25.36 ± 1.64^a	7.32 ± 0.45^a	3.40 ± 1.77^{ab}	2.61 ± 0.76^a	0.83 ± 0.57^a	0.04 ± 0.03^a
Bu	24.12 ± 2.25^a	6.87 ± 1.07^{ab}	3.36 ± 1.05^{ab}	7.22 ± 5.11^b	1.17 ± 1.69^a	0.40 ± 0.22^a
Pe	24.15 ± 3.15^a	6.47 ± 1.08^b	5.00 ± 1.27^a	6.85 ± 6.19^b	1.20 ± 0.47^a	0.22 ± 0.38^a
Pm	24.36 ± 1.92^a	7.26 ± 0.46^a	2.24 ± 1.57^b	7.99 ± 5.49^b	21.11 ± 35.12^b	4.64 ± 5.02^b

*Means within a column followed by the same letter are not significantly different at 5% level

sfrom 6.47 to 7.44 where the highest mean pH was recorded in S2 while the lowest pH was recorded in Pe. Mean pH values were significantly lower at Pe when compared to four other stations (S2, S3, S4 and Pm, $0.044 \leq P \leq 0.018$). The lower pH at Pe is attributed to the acidic nature of fish feces and fish feed and the higher ammonium content that is often found in fish farm effluent [14]. Autotrophic bacteria consume oxygen to oxidize ammonium to nitrite and nitrate which consequently releases hydrogen ions [15] resulting in lower pH.

The mean DO measured ranged from 2.24 to 5.00mg/L. Pe recorded the highest DO attributable to the higher algae growth due to fish aquaculture found in the tributary. The higher algae content suggests that eutrophication is accelerated whereby it causes diurnal fluctuations in DO concentrations [16]. Mean DO at Pm on the other hand recorded the lowest DO due to the animal farm effluent discharged into the tributary. This is in coherence with the study by Ling *et al*. [17] where DO was reported to be lower in the tributary receiving animal farm effluent. The low DO measured was most likely due to the increased microbial activity where microorganisms use up oxygen to degrade the elevated organic matter in the river [2, 17, 18].

The highest BOD_5 values was in Pm (7.99 mg/L), followed by Bu (7.22 mg/L) and Pe (6.85 mg/L). The mean BOD_5 values ranged from 1.86 to 7.99 mg/L and both stations ($P = 0.020$) and dates ($P = 0.037$) significantly affected BOD_5. This is because of heavy rainfall bought about by north east monsoon. BOD_5 mean values at the tributary stations were significantly higher than all the stations along the main river ($0.046 \leq P \leq 0.014$). The higher oxygen demand in Bu was most likely due to the elevated nutrients content caused by fertilizer runoff from the agricultural land located along Bukah River. According to Turner and Haygarth [10], fertilizers introduce higher nutrient content which can lead to higher plant and algal growth. The subsequent decay of the aquatic plants and algae can result in lower DO and higher BOD [11]. The higher demand in Pe on the other hand concurs with previous studies that fish farms have higher BOD [8, 9, 19]. The higher oxygen demand was caused by decomposition of organic matter including microbial respiration of feces and waste feed [20]. The higher demand at Pm was most likely caused by the animal farm effluent discharge which elevated the nutrient and organic matter in the tributary [2, 4, 17]. The study of animal farm oxidation pond efficiency around that area indicated that BOD_5 values of effluent ranged from 8.2 mg/L in the 3-pond system to 82.6 mg/L in the 2-pond system and that the effluent was still high in nutrients [18]. The higher nutrient content elevates the plant and algae biomass that can result in algal blooms that decreases the DO and escalates the demand [4]. The higher organic matter content prompts the rapid growth of microorganisms [5]. The microorganisms rapidly consume oxygen in order to degrade the organic matter in the tributary which then results in a higher oxygen demand [2].

Mean Org-P ranged from 0.45 to 21.1 mg/L where the highest value was recorded in Pm and the concentration at station Pm was significantly higher than the rest of the stations ($P < 0.050$) (Table 1). Pm also recorded the highest Inorg-P value (4.64 mg/L) while the rest of the stations ranged from 0.04 to 0.40 mg/L and the mean value at station Pm was significantly different from all the other stations ($P < 0.050$). The high Org-P and Inorg-P content measured in station Pm was consistent with previous studies which reported that animal farm effluent elevates nutrient content, especially P, N and K in receiving waters [3, 5]. The study of animal farm oxidation pond efficiency indicated that total phosphorus concentration flowing into oxidation ponds ranged from 157 to 258 mg/L whereas in the pond outflow it ranged from 12.2 mg/L in the 3-pond system to 96.3 mg/L in the 2-pond system without solid-liquid separator [18]. The exceptionally high concentrations at Pm also suggested that an overflow of oxidation ponds could have occurred at the animal farms as some of the sampling dates coincided with high precipitations and oxidation ponds were likely not able to contain the surge in inflow due to their small size and

Table 2:Mean values of different forms of nitrogen of the seven sampling stations

	Mean concentration (mg/L)			
Station	TAN	NO_3^--N	Org-N	TKN
S1	0.11±0.08[a]	0.02±0.02[a]	0.92±0.72[a]	1.03±0.65[a]
S2	0.16±0.06[a]	0.04±0.04[ab]	1.19±0.55[a]	1.35±0.54[a]
S3	0.27±0.19[a]	0.05±0.04[abc]	0.99±1.17[a]	1.26±1.10[a]
S4	0.16±0.09[a]	0.05±0.03[abc]	0.91±0.58[a]	1.07±0.61[a]
Bu	0.35±0.13[a]	0.09±0.07[c]	0.24±0.24[a]	0.59±0.18[a]
Pe	0.19±0.08[a]	0.01±0.02[a]	0.66±0.55[a]	0.85±0.47[a]
Pm	2.61±1.75[b]	0.08±0.02[bc]	3.90±5.64[b]	6.51±7.06[b]

Means within a column followed by the same letter are not significantly different at 5% level

Table 3: Mean values of different trace metals of the seven sampling stations

	Mean concentration (μg/L)					
Station	Ni	Zn	Pb	Cd	Cu	Cr
S1	11±5[a]	85±61[a]	18±10[a]	2±2[a]	14± 6[a]	24±31[b]
S2	12±2[ab]	119±94[a]	114±222[a]	4±6[a]	84± 143[a]	7± 7[a]
S3	15±3[abc]	100±76[a]	75±98[a]	5±6[a]	28± 25[a]	5± 1[a]
S4	14±4[ab]	128±115[a]	45±59[a]	2±1[a]	26± 25[a]	5± 1[a]
Bu	18±4[bc]	79±64[a]	23±16[a]	4±1[a]	12± 4[a]	6± 4[a]
Pe	20±2[c]	95±39[a]	48±55[a]	13±12[b]	22± 20[a]	7±3[a]
Pm	18±0[bc]	68±37[a]	18±6[a]	2±1[a]	96± 126[a]	7± 3[a]
Drinking water standard						
USA[*]	-	-	15	5	1300	100
WHO[**]	20	3000	10	3	2000	50

Means within a column followed by the same letter are not significantly different at 5% level

[*]Maximum Contaminant Level, USEPA [34]

[**]Guideline value, WHO [35]

large volume of sludge [18]. January 10 recorded the highest precipitation (187.0 mm) in the month of January while March 13 recorded the second highest precipitation (53.8 mm) in the month of March according to the Sarawak Meteorological Department. High rainfall has been reported to cause overflows which subsequently pollute receiving waters with animal wastewater [21].

In addition, nitrogen analyses results indicated that the Pm station had highest mean TAN, Org-N and TKN concentrations (Table 2) and were significantly higher than other stations ($P \leq 0.038$). This is most likely due to the wastewaters discharged from the pig farm which contains high concentrations of N containing compound [5]. Furthermore, Olajire and Imeolparia [22] and Tchobanoglous *et al*. [23] reported that one of the main sources of TAN is animal farming. According to the study of oxidation pond effluent from pig farms with different ponds systems, total nitrogen was reported to range from 45.6 to 177.9 mg/L [18]. High proportions of Org-N was also found at S1 which was near the village (89.3%), S2 (88.1%) and S4 (85%). The village and human activities nearby those stations have likely contributed to the higher Org-N concentrations. At the Bu station, the lowest proportion (40.7%) of Org-N and the highest concentration of NO_3-N (0.09 mg/L) were observed. This was most likely contributed by the inorganic nitrogen fertilizer used in the agricultural land located along Bukah River delivered to the river through runoff.

The mean concentrations of heavy metals are shown in Table 3. The abundance of trace metals in the stations were in decreasing order of Zn>Pb>Cu>Ni>Cr>Cd. Among the stations, mean metals concentrations were in decreasing order of S2>S3>S4>Pm>Pe>S1>Bu.

Ni concentrations were the highest at the three tributary stations where Pe was the highest followed by Pm and Bu. Ni at Bu is attributable to phosphate fertilizers used for crops [24]. Different plant constituents in animal feed and minerals were reported to contain Ni [7]. Therefore, it is not surprising that those tributaries with animal (chicken, pig and fish) farming have higher concentrations of Ni than the other stations on the main river.

Table 4: Principal component analysis extracted values of various factor analysis parameters for the 7 sampling stations

	Total variance explained before rotation			Total variance explained after rotation		
	Extraction sums of squared loadings			Rotation sums of squared loadings		
Component	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	2.10	34.95	34.95	2.00	33.31	33.31
2	1.94	32.33	67.28	1.95	32.48	65.79
3	1.21	20.24	87.52	1.30	21.73	87.52

The highest concentration of Zn was found in S4 followed by S2. Both stations with high Zn content were near the area of heavy traffic, by the road side. Davis *et al*. [25] reported that automobile brakes, tires and engine oil contributed Zn, Cu, Pb and Cd the most abundant of which was Zn. The high Zn at both stations could also be due to the corrosion of the metal bridges as Zn is commonly used for galvanizing iron and steel [26]. Station S2 has much higher Pb and Cu than S4 likely due to recreational fishing practised by locals near that station. The higher Pb is likely due to vehicular contribution and angling equipment which has been reported to contain lead in various components such as weights, split shots, pirks and downriggers [27]. Lead fishing weights may be lost into streams and corrode into more toxic forms besides increasing the Pb concentration in receiving waters [27, 28]. Near station S2, there was a bridge and vehicles had to apply brake which probably contributed more Pb than station S4. Since Pm showed the lowest Pb concentration, the high levels of Pb found in S3 could be attributed to the waste found near the sampling station where old computers, glass bottles and old tyres had been discarded and contributions from station S2. Computers often contain trace metals such as Pb [29] which could account for the increased Pb concentration in S3.

Cu was the highest at station Pm, downstream of pig and chicken farm and Cd was the highest at Pe where fish were cultured. This is most likely due to the addition of Cu to animal feed and Cd could be present in feed due to plant uptake of Cd from the agricultural land [7]. As a consequence, animal faeces and urine contained large amount of Cd and Cu [30-32]. Menduguchia *et al*. [33] reported that samples of fish feed presented high levels of Zn and Cu and low concentration of Pb and Cd was found in fishmeal [7]. The highest Cr concentration was detected at S1 which might be due to the corrosion of steel and iron from the school and village buildings which were located near to this station. According to McGrath [24] steel and iron are major anthropogenic source of Cr as Cr is used in alloy steels and the proportion was reported to be 10-26%. Even though Pm was the highest in BOD_5, Org-P, Inorg-P, TAN, the concentrations of Ni, Zn, Pb and Cd were not higher than that of Pe. This is likely due to the treatment of wastewater by oxidation ponds in the animal farms [18]. As a result, some metals might have been retained in the oxidation ponds.

Factor analysis indicates that there are three components with eigenvalues > 1 and they explained 87.5% of the total variance in the heavy metals measured (Table 4). The three component scores are expressed in equations [1,3].

$$C_1 = 0.87\, Pb + 0.85\, Zn - 0.23\, Cr - 0.64\, Ni - 0.22\, Cd + 0.34\, Cu \quad [1]$$

$$C_2 = 0.34\, Pb + 0.14\, Zn - 0.83\, Cr + 0.75\, Ni + 0.73\, Cd + 0.12\, Cu \quad [2]$$

$$C_3 = 0.05\, Pb + 0.39\, Zn + 0.25\, Cr - 0.13\, Ni + 0.46\, Cd - 0.87\, Cu \quad [3]$$

The first component accounted for 33.3% of the variation and was positively correlated with Pb and Zn. This component indicates vehicular contribution. The second component accounted for 32.5% of the variation and was positively correlated with Ni and Cd but negatively correlated with Cr. The higher the score of this component, the more likely it is associated with agriculture where chemical fertilizers were used. The negative correlation with Cr indicated that the lower the score, the more likely the station is involved in human settlement such as villages and schools. The third component accounted for 21.7% of the total variation and it was negatively correlated with Cu indicating that the lower the score, the more likely the station is involved with animal and fish farming.

Comparisons with drinking water quality criteria indicate that NO_3-N concentrations (Table 2) complied with the Maximum Contaminant Level (MCL) of 10 mg/L set by USEPA [34] (Table 3). For trace metals, Ni, Cu and Cr complied with both WHO guideline value [35] and MCL set by USEPA [34]. For Cd, all the stations complied with MCL of USEPA except the Pm station. For Pb, concentration at all stations exceeded the MCL of USEPA [34].

CONCLUSIONS

DO of the Serin River at most of stations were below the minimum required for healthy aquatic life. Organic matter and nutrients parameters were higher nearby areas of animal farming, fish farming, agricultural crops and residential areas. Trace metals were also impacted by such activities. Tributaries showed the higher organic matter, nutrients and some of the trace metals than the main river. Stations by the road showed high zinc, lead and copper indicating the impact of vehicles on trace metals in the river. Principal component analysis classified the heavy metals. Effluent from animal and fish farms need to be treated, solid waste need to be recycled and stormwater need to be treated to protect the water quality.

ACKNOWLEDGEMENT

The authors acknowledge the financial assistance provided by Universiti Malaysia Sarawak and the Malaysian Ministry of Science, Technology and Innovation (e-sci 06-01-09-SF0026).

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