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Evaluation of Sewage Pollution in the Linggi River Water using Hydrochemical Parameters

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Sewage pollution in the river water ecosystem has created many environmental problems worldwide. Hydrochemistry studies on river water have been used as a promising tool to comprehend the sewage pollution status in freshwater. This study examines the concentration of anions (nitrate, sulfate, phosphate, fluoride, and chloride) and cations (sodium, potassium, magnesium, and calcium) in the river water samples during the dry and rainy seasons. The determination of anions and cations was carried out using established American Public Health Association (APHA) methods. From the results, alkalinity was the highest parameter during both seasons, with the mean value of 35.73 ± 13.63 and 17.28 ± 6.26 mg L^{-1} during the dry and rainy seasons, respectively. The correlation between nitrate and chloride revealed diverse anthropogenic sources including sewage during the dry season than the rainy season. On the other hand, the correlation between sodium and chloride indicates significant natural input during the dry season and significant sewage input during the rainy season in the Linggi River. Further chemical and biological analysis must be examined to complement the hydrochemical parameters towards better assessment of sewage pollution in the river water.

Keywords: River water; cations; anions; hydrochemical; sewage pollution

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Globally, aquatic systems are subject to increasing anthropogenic input, leading to substantial deterioration of water quality. Various anthropogenic activities, such as sewage, discharge into freshwater and coastal waters have become an alarming issue in recent years [1]. Sewage effluents are released into streams, lakes, estuaries, and groundwater, and some chemical compounds in these effluents affect water quality and aquatic life. In addition, an increasing volume of sewage produced by the growing population without the necessary infrastructure for collection, treatment, and appropriate disposal poses a tremendous threat to receiving waters [2,3]. These phenomena will further alter the hydrochemical characteristics of the freshwater ecosystem.

Hydrochemistry of water, such as river water and groundwater, is a result of long-term interactions between the water body and the surrounding environment through the water cycle, which involved the processes of water formation and movement [4–6]. The water cycle depends on various factors, such as the hydrological conditions of rivers, aquifers, and oceans as well as anthropogenic activities. Surface runoff, effluent discharge, urbanization, and agricultural activities may contribute to changes in the hydrochemistry of water samples in the environment.

Among the hydrochemical parameters, cations (calcium, magnesium, potassium, and sodium) and anions (chloride, nitrate, sulfate, phosphate, and fluoride) are among the major ions in river water [7–9]. Fluctuations in cations and anions indicate the contributions of anthropogenic activities, such as industrial effluent discharge, agricultural runoff, urbanization, and sewage and domestic waste deposition [10–12]. For instance, cations such as calcium, magnesium, sodium, and potassium represent water-rock interactions [13,14]; however, these ions are also derived from anthropogenic sources. Furthermore, abundant phosphates and chlorides may be derived from fertilizer waste [11,15] and sewage [16,17]. Therefore, the assessment of the hydrochemical parameters in the river water may help in understanding the sewage

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pollution in the river water. The objective of this study is to understand the sewage pollution input in the Linggi River by using the hydrochemical parameters of selected anions and cations. This study will aid the environmental related agencies in Malaysia in the pollution mitigation action plans by using the hydro-chemical parameters of the major river obtained from the National River Water Monitoring Program.

METHODOLOGY

Study Area

Linggi River is located in the Negeri Sembilan state and covers a distance of approximately 1,530 km^2. The river passes through urban areas, such as Seremban and Senawang, as well as rural areas, toward the Strait of Malacca. The Linggi catchment is dominated by residential and industrial areas in the upstream region, while major agricultural activities, small residential areas, and drinking water intake point are located from the middle stream toward the downstream areas. The sampling locations for this study was shown in Figure 1.

Sampling Procedures

Sampling was conducted in November 2017 (rainy season) and April 2018 (dry season) at Linggi, Negeri Sembilan. All samples were collected in duplicate from river water samples (RW1, RW2, RW3, RW4, RW5 and RW6) (Figure 1). To understand the hydrochemical parameters correlation with sewage pollution, the river water samples were collected after the discharge point from nearby sewage treatment plants (STPs). A detailed description of the sampling sites is listed in Table 1.

For hydrochemical analysis, river water samples were collected using a clean bucket and passed through a 0.45-µm membrane filter. The samples were stored in 250 mL bottles for anion (nitrate, sulfate, phosphate, fluoride, and chloride) analysis. For cation (sodium, potassium, magnesium, iron, and calcium) analysis, the samples were preserved in nitric acid: deionized water (1:1) solution until the pH fell below 2 and stored in the 250 mL of bottles. All samples for hydrochemical analysis were stored in an icebox and kept in a refrigerator at ±4 °C in the laboratory. All samples were analyzed within 1 month (for cations) or 48 h (for anions) of collection.

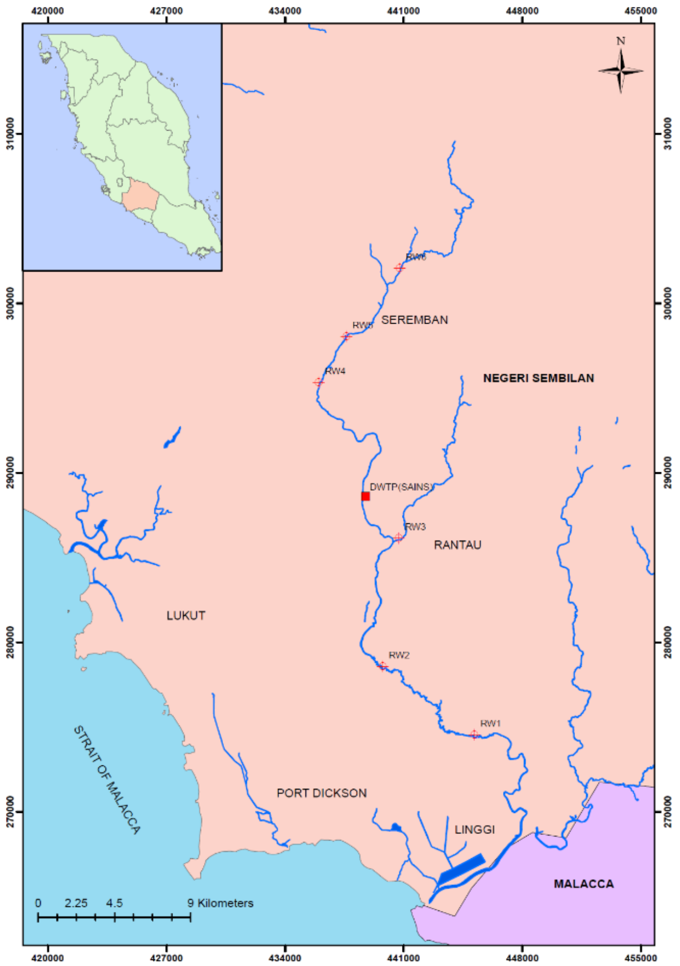

Figure 1. River water sampling location at Linggi River

Table 1. Description of the sampling locations

No	Sampling sites	Town/Area	Land use/STP type
1	RW1	Linggi town	Small town, cow farm
2	RW2	Taman Desa Port Dickson	Housing area, STP
3	RW3	Rantau	Palm oil plantations, small town, housing
4	RW4	Sungai Ara	Small housing area
5	RW5	Mantau	Small housing area
6	RW6	Ampangan	Large housing area, goat farm

Analysis of Anions

Nitrate, sulfate, phosphate, fluoride, and chloride in the water samples were simultaneously detected using Ion Chromatography (IC) (Brand: Dionex) following the American Public Health Association (APHA) 4110B method. Briefly, the water samples are injected into a stream of eluent in the IC system and passed through a series of ion exchangers. The target anions are separated based on their relative affinities for a low-capacity, strongly basic anion exchanger in the guard and analytical columns of the IC system. The separated anions are directed through suppressors, which continuously suppress eluent conductivity and promote analyte response. In the suppressor, the separated anions are converted to their highly conductive acid forms, while the conductivity of the eluent is greatly decreased. The separated anions in their acid forms are quantified based on their conductivity and identified based on their retention time. Quantification was performed using the peak area of the ions. Details of the apparatus, reagent, chemicals, standards, and quality controls are described elsewhere [18]. Alkalinity was determined following to the APHA 2320B standard method. Briefly, alkalinity was determined based on the hydroxyl ions present in the sample as a result of the dissociation or hydrolysis of solutes react with acid. The details procedure for alkalinity are described elsewhere [18].

Analysis of Cations

Sodium, potassium, magnesium, and calcium were determined following to the APHA 3125 standard method. Briefly, the water samples are introduced to argon-based, high-temperature radio-frequency plasma via pneumatic nebulization. As energy is transferred from the plasma to the sample stream, the target elements are dissolved, atomized, and ionized. The resulting ions are extracted from the plasma through a differential vacuum interface and separated based on their mass-to-charge (*m/z*) ratio via MS. The collision cell technology with helium gas is used to improve sensitivity. An electron multiplier detector is used to count the separated ions, and a computer-based data-management system is used to process the resulting information. Details of the apparatus, reagent, chemicals, standards, and quality controls are described elsewhere [18].

RESULTS AND DISCUSSION

Descriptive Statistics

The use of hydrochemistry, including cations and anions, under various environmental conditions for evaluating the degree of sewage pollution has been extensively discussed. These analyses enable better interpretation of the current status and estimation of the future water pollution, particularly sewage contamination, to design mitigation actions.

Table 2 presents a summary of descriptive statistics of the hydrochemical parameters of river water samples. In river water samples, alkalinity was the highest parameter during both seasons, with mean of 35.73 ± 13.63 and 17.28 ± 6.26 mg L^{-1} during the dry and rainy seasons, respectively (Table 2). This elevated alkalinity of the river water may be a result of the dissolution of carbon dioxide gas derived from the nitrification, denitrification, and organic matter biodegradation processes in the river water ecosystem [19,20]. Furthermore, the mean of chloride concentration was higher during the dry season (15.79 ±11.17 mg L^{-1}) than during the rainy season (9.90 ± 4.81 mg L^{-1}). Chloride is one of the conventional tracers of sewage in the freshwater environment [16,17]. Therefore, the river water of Linggi is more severely affected by sewage discharge from the nearby STPs during the dry season than during the rainy season.

Table 2. Descriptive statistics for hydrochemical parameters (mg L^{-1}) of river water during the dry and rainy seasons *

Season	Sample type	Statistic	Ca^{2+}	K^+	Mg^{2+}	Na^+	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Alkalinity
Dry Season	River water (n = 12)	Minimum	7.38	3.21	0.57	5.60	0.11	6.52	0.97	0.05	5.45	18.26
		Maximum	20.96	14.76	1.34	24.22	0.88	37.78	36.08	0.05	32.30	55.76
		Mean	12.01	6.42	0.86	10.48	0.34	15.79	11.52	0.05	14.99	35.73
		Variance	19.83	15.96	0.07	45.37	0.07	124.72	166.89	0.00	100.66	185.69
		Standard deviation	4.45	3.99	0.27	6.74	0.26	11.17	12.92	0.00	10.03	13.63
Rainy season	River water (n = 12)	Minimum	6.14	2.23	0.65	2.97	0.10	4.83	2.76	0.05	5.89	7.60
		Maximum	12.95	7.35	1.32	9.49	0.23	17.57	16.76	0.12	15.67	24.70
		Mean	8.67	4.75	0.91	5.31	0.18	9.90	6.97	0.06	8.99	17.28
		Variance	4.11	2.72	0.05	3.91	0.00	23.10	23.10	0.00	10.34	39.23
		Standard deviation	2.03	1.65	0.22	1.98	0.05	4.81	4.81	0.02	3.22	6.26

*(calcium = Ca^{2+}; potassium = K^+; magnesium = Mg^{2+}; sodium = Na^+; fluoride = F^-; chloride = Cl^-; nitrate = NO_3^-; phosphate = PO_4^{3-}; sulfate = SO_4^{2-})

Sewage Pollution using Hydrochemical Parameters

Sources of sewage in river water samples are complex, and the major cations and anions sources can be determined based on the associations of hydrochemical parameters of water samples. For instance, the major sources of nitrate and chloride in freshwater include mineral dissolution, agricultural potassium fertilizers, domestic sewage, and animal feces. The chloride ion is relatively stable in the natural environment and is hardly affected by biogeochemical processes. Preferably, the correlations between nitrate and chloride and between sodium and chloride are used to understand the transformation and potential sources of nitrate in water samples [12].

Figure 2 demonstrates the correlation between nitrate and chloride in river water during the dry (a) and rainy (b) seasons. There was a strong positive correlation (p < 0.05) between nitrate and chloride during the dry (R^2= 0.98) and rainy (R^2=0.82) season. The strong positive correlation between nitrate and chloride during the dry season may due to the similar abundance of nitrate and chloride sources from anthropogenic activities than the rainy season. This positive correlation may be attributed to anthropogenic sources, such as sewage/manure or industrial and domestic waste [21,22]. The abundance of nitrate and chloride has also been reported in manure and sewage samples [16,23]. The moderate correlation of nitrate and chloride during the rainy season also may be due to seasonal factors such as rainfall distribution and humidity during the rainy season. Further, the wider range of nitrate/chloride line in river water samples during the dry season (Figure 2 (a)) than during the rainy season (Figure 2 (b)) indicates more diverse anthropogenic sources in the samples during the former season than during the latter one.

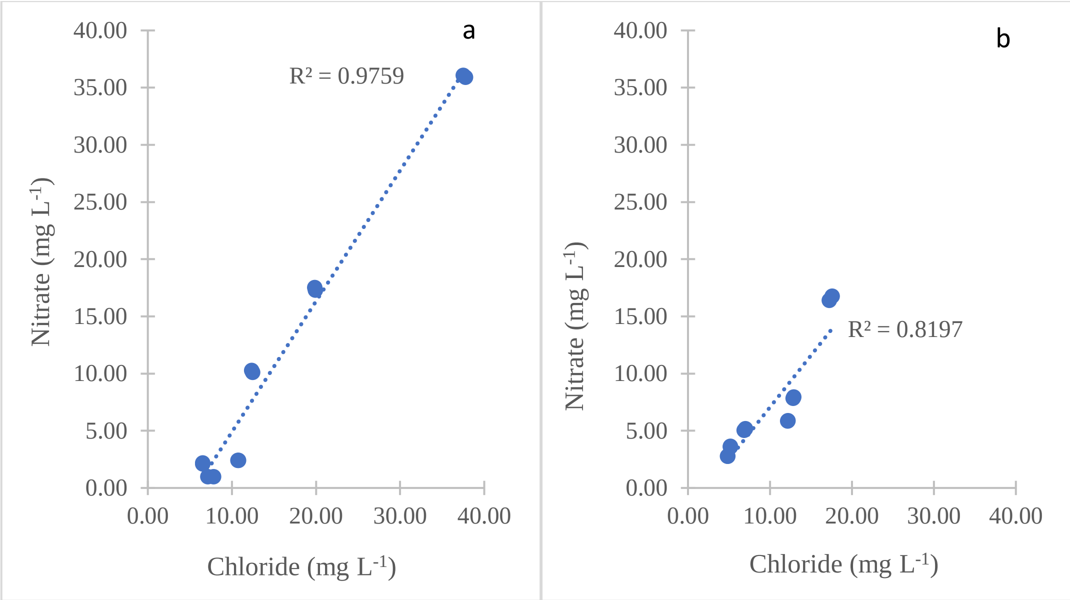

Figure 2. Correlation between nitrate and chloride level in river water samples during the dry (a) and rainy (b) seasons

Figure 3 demonstrates the correlation between chloride and sodium during the dry (a) and rainy (b) seasons. There was a strong positive correlation ($p < 0.05$) between chloride and sodium during the dry season (R^2= 0.98) and a moderate positive correlation ($p < 0.05$) during the rainy season (R^2=0.59). During the dry season, most of the river water samples fell on the 1:1 line, indicating natural input; however, the deviation of some river water samples from the 1:1 line during the rainy season indicates possible anthropogenic influences [24,25]. Excess contribution of sodium and chloride in some river water samples was suspected through the discharge of sewage effluents from STPs and chemical fertilizers from nearby plantations via surface runoff [24,26].

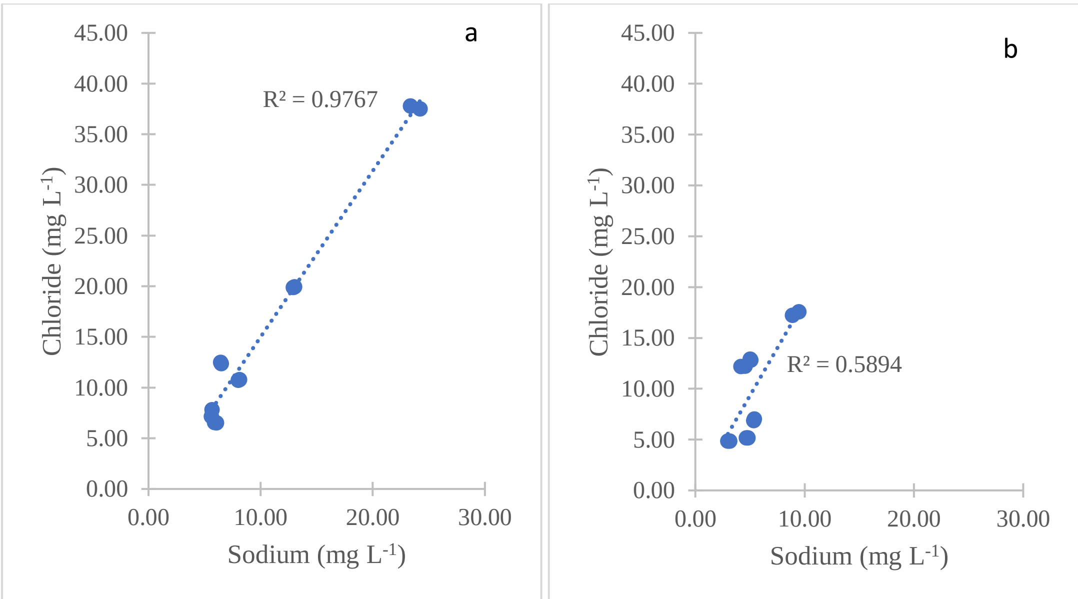

Figure 3. Correlation between chloride and sodium level in river water samples during the dry (a) and rainy (b) seasons

CONCLUSION

The concentration of cations (calcium, potassium, magnesium, and sodium) and anions (fluoride, chloride, nitrate, phosphate, sulfate, and alkalinity) varied in the river water sampling locations during both seasons. Alkalinity was the most dominant parameter in STP, river water, and groundwater samples during both seasons. The dominance of alkalinity in river water samples was due to the dissolution of carbon dioxide from nitrification, denitrification, and organic matter biodegradation in the river water ecosystem. Chloride, which is a conventional tracer for sewage, was detected at higher levels during the dry season than during the rainy season. The correlation between nitrate and chloride results suggests the diverse anthropogenic sources including sewage pollution during the dry season than the rainy season. However, the correlation between sodium and chloride revealed enhanced anthropogenic input including sewage input during the rainy season than the dry season. These contradictions of results between the dry season and rainy season by using the difference of hydrochemical parameters may be due to the seasonal influences, hydrological conditions of the river, surface runoff and the variation of sewage and other anthropogenic input in each sampling stations during both seasons. Such circumstances may lead to the variation of cations and anions discharge into Linggi River Water. Therefore, further analysis of the other sewage molecular markers (such as sterols, stanols, pharmaceutical wastes, and disruptor hormones) and biological parameters (such as bacteria and viruses from sewage) must be supplemented with hydrochemical parameters to understand the sewage pollution sources in the river water for further water pollution mitigation action plans.

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