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ORIGINAL ARTICLE

Elemental hydrochemistry assessment on its variation and quality status in Langat River, Western Peninsular Malaysia

Wan Ying Lim · Ahmad Zaharin Aris ·
Tengku Hanidza Tengku Ismail · Mohamad Pauzi Zakaria

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Abstract This paper discusses the hydrochemistry variation and its quality status in Langat River, based on the chemistry of major ions, metal concentrations and suitability for drinking purposes. Water samples were collected from 30 different stations to assess their hydrochemical characteristics. The physico-chemical parameters selected were temperature, electrical conductivity, total dissolved solids (TDS), salinity, dissolved oxygen , pH, redox potential, HCO_3, Cl, SO_4, NO_3, Ca, Na, K, Mg, ^{27}Al, ^{138}Ba, ^{9}Be, ^{111}Cd, ^{59}Co, ^{63}Cu, ^{52}Cr, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{80}Se and ^{66}Zn to investigate the variation of the constituents in the river water. Most of the parameters comply with the Drinking Water Quality Standard of the World Health Organization and the Malaysian National Standard for Drinking Water Quality by the Malaysia Ministry of Health except for EC, TDS, Cl, HCO_3, SO_4, Na, Mg, Al, Fe and Se. The results show that the Langat River is unsuitable for drinking purposes directly without treatment.

Keywords Langat River · Surface water · Hydrochemistry · Variation of constituents · Guidelines

Introduction

River ecosystems are one of the important assets based on their immense biological diversity. Numerous interactions between different forms of plant and animals can be found in the river ecosystems. Thus, river ecosystems are highly regarded for their biological productivity and high accessibility. Hence, the high economic values of these ecosystems make them suitable for aquaculture activities, a source of food for sustaining food security, recreation, ecotourism and as a genetic resource. Due to the rapid development in aquaculture and fishing activities, heavy metals are released or leached into the environment, which has contributed to the degradation and destruction of the ecosystem. The accumulation of metals in the environment is due to the fact that they cannot be broken down, unlike the organic pollutants that can be degraded to carbon dioxide and water (Gupta et al. 2001; Khan et al. 2004). When metals enter the environment, they will be incorporated in the soils with organic matter, Fe/Mn oxides, sulfides, and clay (Wang and Chen 2000), thus, forming several reactive components that are harmful to the environment. Certain metals, which are potent toxins enter the food chain through phytoplankton and are biomagnified in fish or other aquatic organisms (Andrews et al. 2009). As a result, food sources from rivers that are contaminated with metals pose a potential human health risk. The natural resources and overall environment of a river will become detrimental once the water quality is depleted (Ujang et al. 2008). Hence, human activities bring not only development but also contamination. Despite the importance of the river ecosystems, the release of pollutants, such as heavy metals into the environment attributed to dense development has become an emerging issue to river ecosystems, food security, and their ecological balance (Mokhtar et al. 2009b).

The development activities in Malaysia involving manmade alterations of the river environment have accelerated the impact of pollution leading to the deterioration of river quality, depletion of river resources, public health

W. Y. Lim · A. Z. Aris (✉) · T. H. T. Ismail · M. P. Zakaria
Environmental Forensics Research Centre,
Faculty of Environmental Studies, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia
e-mail: zaharin@env.upm.edu.my

risks and loss of biodiversity. Langat River is the principal river draining the densely populated and developed area of Selangor (Sarmani 1989; Mokhtar et al. 2009b). It serves about 50 % of the population of Selangor by providing potable water to residents and also supplies water for the manufacturing and agricultural industries. Langat River plays a significant role in the ecology and other services, such as recreational sites, habitats for fish and other aquatic wildlife. The land area within the basin, especially from the middle to the lower stream of the river, has been widely exploited to support the expanding population growth. In addition, poor land-management practices along the river basin have increased the pollution loading into the river. Several researches have been conducted to assess the status of heavy-metal contamination or water quality within the Langat River Basin (Sarmani 1989; Azrina et al. 2006; Bahaa-Eldin et al. 2008; Mokhtar et al. 2009b; Franklin et al. 2010). Several studies revealed that the pollutants are from industrial, urban or agricultural activities (Sarmani 1989; Azrina et al. 2006; DOE 2009; Mokhtar et al. 2009b). As, Cd, Co, Ni, Pb and Zn concentrations at Langat River have generally been found to be higher compared to other elements. Langat River is acknowledged to be one of the most polluted rivers in the state of Selangor (Sarmani 1989; DOE 2009). This is mainly due to the rapid industrialization and urbanization arising from the development of the infrastructure and expanding population.

This study focuses on the downstream section of the Langat River, because this area receives the maximum contaminant discharges from upstream and tributaries that flow through the hub of the industrial, residential and commercial areas within the basin. It aims to assess the water chemistry variance by determining the in situ parameters [temperature, electrical conductivity (EC), total dissolved solids (TDS), salinity, dissolved oxygen (DO), pH and redox potential (*Eh*)], major ions (HCO_3, Cl, SO_4, NO_3, Ca, Na, Mg and K) and metals (^{27}Al, ^{138}Ba, ^{9}Be, ^{111}Cd, ^{59}Co, ^{63}Cu, ^{52}Cr, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{80}Se and ^{66}Zn) concentrations in Langat River. The obtained results are compared with the Malaysian National Standard for Drinking Water Quality (NSDWQ) by the Ministry of Health (MOH 2004) and Drinking Water Quality Standard of the World Health Organization (WHO 2004). These results can provide a baseline for future monitoring and tracking of changes in water quality due to human activities within this basin.

Materials and methods

Study area

The Langat River Basin is located in the mid-western part of Peninsular Malaysia running across two states, Selangor and Negeri Sembilan. The basin lies between latitudes 2°40′152″N and 3°16′15″N, longitudes 101°19′20″E and 102°1′10″E with a total catchment area of approximately 1,815 km^2. The main river course is 141-km long and is mostly situated 40 km east of Kuala Lumpur. The river flows from the high hills in the north toward the plains and turns westward toward the coast of the state of Selangor (Mokhtar et al. 2009b). The basin consists of two estuaries, one is located on the northeastern side and the river water flows into the Lumut Strait while the other is on the southern side and flows directly into the Strait of Malacca (Mokhtar et al. 2009b). Langat River receives an annual rainfall of 1,500–2,900 mm, which is influenced by the monsoon in November and January. The basin experiences an average temperature of 32 °C with a relative humidity of 80 %. A summary of the monthly rainfall from 2000 to 2009 for the study area is shown (Fig. 1).

The Langat River Basin can be divided into three areas; the mountainous area, the hilly area and the lowlands. The Langat River and its major tributary, the Semenyih River, originate on the western slope of the mountain ridge penetrating the Malay Peninsula. The river flows generally southwestward in the mountainous terrain (Gunung Nuang) in the north toward the hilly area. The lower part of the hilly area covers Cyberjaya, Dengkil and Kuala Lumpur International Airport (KLIA) (JICA and MGDM 2002). The basin is covered by different soil series; the hilly area (upstream) mostly is covered by Steepland–Serdang series, while the lower area (downstream) covered by other soil series such as Serdang–Bungor–Munchong series (clay loam), Selangor–Kangkong series (clay and silt), Munchong–Seremban series (fine sandy clay), and Keranji series (clay) (JICA and MGDM 2002). The basin is underlain by schist, phyllite and granite rock formation of Permian age. Bedrock in the mountainous area consists of schist and phyllite of Hawthornden formation in Old Silurian and Permian igneous rocks (Gobbett and Hutchison 1973). Bedrock in the hilly area is predominantly with permo-carboniferous meta-sandstone, consisting of mainly quartzite and slates of Kajang formation and Kenny Hill formation (Gobbett and Hutchison 1973; Taha 2003). The lowland area, an alluvial plane, is located in the southwestern part of the Langat basin. It is bounded by the hilly area to the north and east and by the sea to the southwest. The riverbed sediments change composition gradually from gravel in the mountainous area to sand, and then, silt in the hilly area to be clayey at Banting (JICA and MGDM 2002). The study area is located in the low flat alluvial plain close to the coast and occupied by the young alluvial sediment (Gobbett and Hutchison 1973; Taha 2003). They have been deposited under fluviatile or marine sedimental conditions to fill undulations of the bedrock of the Kenny Hill formation and Kajang formation (JICA and MGDM

2002). The Quaternary deposits are made up of marine and continental deposits and consist of clay, silt, sand peat with minor gravel (JICA and MGDM 2002; Taha 2003; Mohamed et al. 2009).

Field sampling and preservation

The sampling was carried out in December 2010 and 30 sampling stations were chosen (Fig. 2; Table 1). Stations LY1–LY14 are located downstream and near to the estuary and LY15–LY30 are located upstream. All the laboratory apparatus were pre-cleaned with acid wash and soaked overnight in 5 % (v/v) concentrated nitric acid (HNO_3) and were rinsed thoroughly with deionised water to ensure any contaminant and trace of cleaning reagent were removed before the analysis (APHA 2005). Polyethylene bottles were used for collecting water samples to avoid and minimize interference during heavy-metal analysis. During sampling, the polyethylene bottles were normalized by rinsing with the water to be collected several times and then filled with running water facing the direction of flow. Triplicate samples were collected and homogenized from each sampling station. Each bottle was labeled with its corresponding sampling station and time of sampling. Samples were kept at 4 °C and transported back to the laboratory to minimize the microbial activity in the water (APHA 2005).

Water analysis

Multi-parameter probes (SevenGo pro probe and SevenGo Duo pro probe, Mettler Toledo AG, Switzerland) were used to conduct in situ measurement of conductivity, TDS, salinity, *Eh* and pH. The temperature and DO were measured using an YSI 52-dissolved oxygen meter (YSI Inc., Yellow Springs, Ohio, USA). All probes were calibrated prior to sampling. Bicarbonate (titration method using 0.02 N HCl) and chloride ions (argentometric method using 0.0141 N $AgNO_3$) were analyzed on site using unfiltered samples (APHA 2005). The samples were filtered with a 0.45 μm cellulose acetate membrane filter (Whatman Milipores, Clifton, NJ, USA) to obtain dissolved metal while avoiding the occurrence of clogging during analysis with spectrometry instruments. Each sample was then separated into two polyethylene bottles, one for subsequent analysis of sulfate (SurfaVer4 HACH method) and nitrate (NitraVer5 HACH method) and the second bottle was for determination of cations (Ca, Na, Mg and K) and trace elements (^{27}Al, ^{138}Ba, ^{9}Be, ^{111}Cd, ^{59}Co, ^{63}Cu, ^{52}Cr, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{80}Se and ^{66}Zn) (HACH 2003; APHA 2005). To prevent precipitation of components, such as metal oxides and to retard any biological activities, the second bottle was preserved through acidification by HNO_3 to $pH < 2$. Major cations (Ca, Na, Mg and K) were analyzed using Flame Atomic Absorption Spectrometry (FAAS, Shimadzu AA6800, Shimadzu Scientific Instruments, Kyoto, Japan) while trace metals (^{27}Al, ^{138}Ba, ^{9}Be, ^{111}Cd, ^{59}Co, ^{63}Cu, ^{52}Cr, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{80}Se and ^{66}Zn) were analyzed using Inductive Couple Plasma Mass Spectrometry (ICP-MS, ELAN DRC-e, Perkin Elmer, Waltham, MA, USA).

Quality assurance and quality control (QA/QC)

All reagents used were of analytical grade or equivalent and free from any contaminants that may have interfered with the analysis. The laboratory apparatuses were cleaned with 5 % (v/v) HNO_3 and then rinsed with distilled water. Stock standard solutions of each element were used to prepare calibration solutions to obtain calibration curves. The selected physico-chemical parameters and heavy-metal analyses were recorded as mean ± standard deviation (SD) of triplicate measurements. Blanks were also determined and used for background correction. The concentration of trace metals was expressed as micrograms per liter (μg/L) and milligrams per liter (mg/L) for cations. The

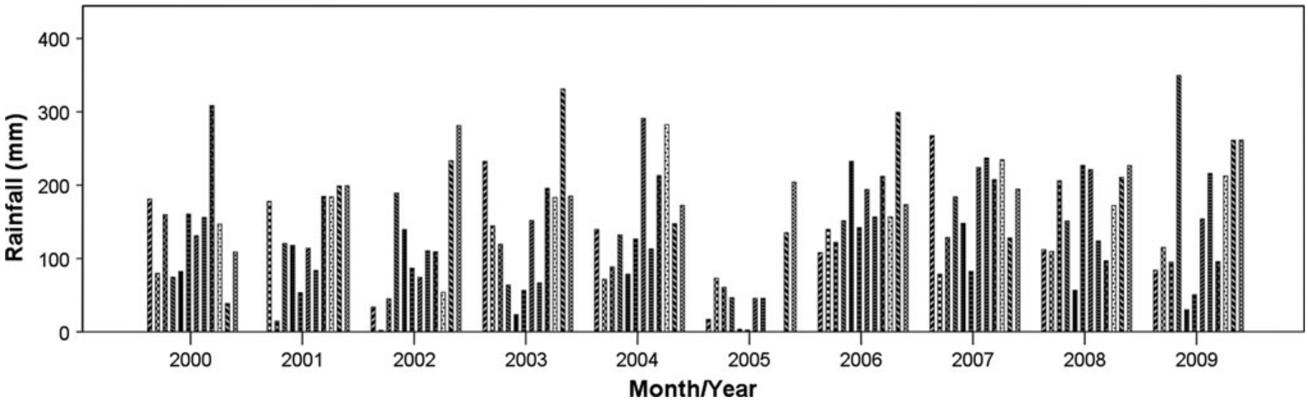

Fig. 1 Monthly rainfall data (Jan–Dec) of study area from 2000 to 2009

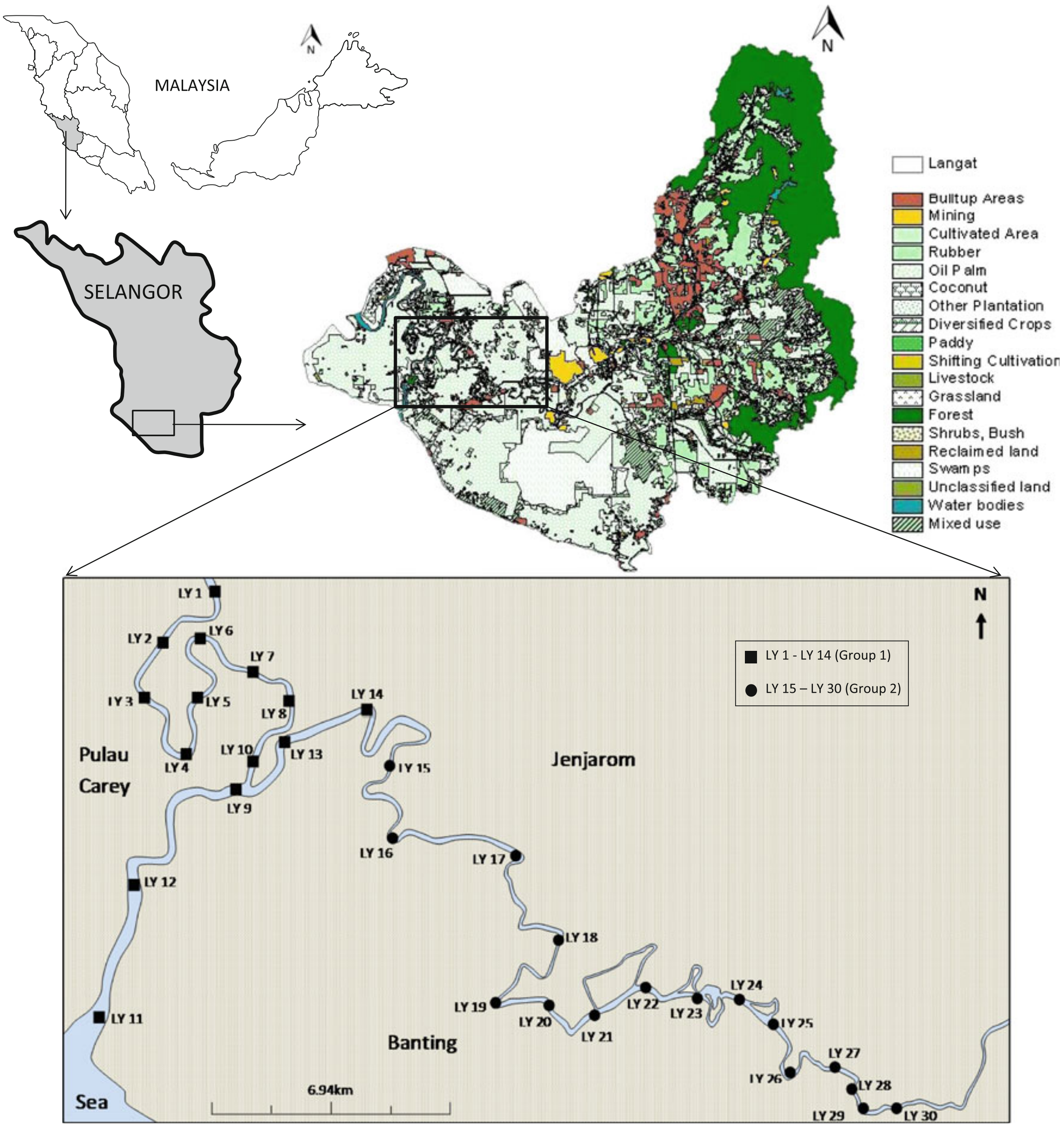

Fig. 2 Map of sampling stations in Langat River

recovery rate was between 95 and 105 % (±5 %) depending on the element analyzed, as shown in Table 2.

Data analyses

ANOVA was applied to test the significant difference for all water quality variables among stations. A Post hoc test was performed using the LSD test with a degree of significance at 0.05. The Pearson correlation coefficient (*r*) was performed to see the relationship between physico-chemical parameters and ions. All statistical analyses were performed using PASW Statistics 18 (formerly known as SPSS Statistics 18 or SPSS Base).

Results and discussion

Table 3 shows the descriptive statistics for the selected physico-chemical parameters and heavy-metal concentrations. The coefficient of variance (CV) calculated on the selected parameters revealed that the data of all parameters varied from the mean with a CV value higher than 50 % except for pH and temperature. The high CV implied that recorded readings for most parameters varied from station to station. The variations were more pronounced in the downstream area (LY1–LY14). The downstream stations which were near to the estuary, experienced a higher seawater exposure.

Table 1 The coordinate of sampling stations

Station	Latitude	Longitude
LY1	2°55′12.16″N	101°25′49.98″E
LY2	2°54′18.20″N	101°25′04.93″E
LY3	2°53′24.43″N	101°24′48.25″E
LY4	2°52′31.16″N	101°25′33.20″E
LY5	2°53′25.51″N	101°25′40.92″E
LY6	2°54′26.50″N	101°25′39.71″E
LY7	2°53′53.38″N	101°26′33.14″E
LY8	2°53′28.28″N	101°27′08.59″E
LY9	2°51′59.68″N	101°26′23.10″E
LY10	2°52′28.37″N	101°26′37.31″E
LY11	2°48′14.80″N	101°24′26.80″E
LY12	2°50′23.60″N	101°24′51.70″E
LY13	2°52′47.50″N	101°27′06.00″E
LY14	2°53′23.10″N	101°28′23.60″E
LY15	2°52′32.20″N	101°28′46.40″E
LY16	2°51′19.50″N	101°28′55.00″E
LY17	2°51′10.70″N	101°30′53.50″E
LY18	2°49′51.30″N	101°31′37.50″E
LY19	2°48′47.60″N	101°30′40.40″E
LY20	2°48′47.30″N	101°31′33.50″E
LY21	2°48′41.20″N	101°32′15.20″E
LY22	2°49′08.00″N	101°33′02.10″E
LY23	2°49′04.80″N	101°33′50.30″E
LY24	2°49′00.30″N	101°34′34.20″E
LY25	2°48′41.40″N	101°35′03.80″E
LY26	2°47′56.40″N	101°35′22.30″E
LY27	2°48′04.80″N	101°36′04.10″E
LY28	2°47′43.50″N	101°36′19.60″E
LY29	2°47′27.38″N	101°36′33.42″E
LY30	2°47′25.20″N	101°36′51.40″E

Table 2 Percentage recoveries of trace metals by ICP-MS

Metals	Recovery (%)	Detection limit ranges (ppt)
Al	100.28	1–10
Ba	99.01	<0.1–1
Cd	102.05	1–10
Cu	101.87	1–10
Fe	98.46	1–10
Pb	102.12	<0.1–1
Mn	97.57	1–10
Zn	101.97	1–10
Co	100.53	1–10
Be	103.08	1–10
Cr	101.53	1–10
Ni	101.72	1–10
Se	103.43	10–100

Physico-chemical parameters

The pH value ranged from 4.47 (LY1) to 7.48 (LY11), with an average value of 6.67 ± 0.53. All analyzed samples were well within the limits prescribed by MOH (6.50–9.0) and WHO (6.5–9.2) except for LY1. The acidic condition at certain sampling stations (closer to mangrove or plantation areas) may be attributed to the carbonic acid formed during the photosynthetic process by water plants (Eqs. 1, 2). Other factors included the presence of substantial amount of organic matter in the study area (Mokhtar et al. 2009a; Radojević and Bashkin 2007). The transfer of hydrogen ion (H^+) between chemical species determines the pH of the aqueous solution. The increased hydrogen ion concentration in natural water as a consequence of cation exchange had reduced the pH to a certain extent (Radojević and Bashkin 2007)

$$H_2O + CO_2 \rightarrow H_2CO_3, \tag{1}$$

$$H_2CO_3 \rightarrow 2H^+ + CO_3^-. \tag{2}$$

In contrast, the alkaline condition noted at certain sampling stations might be explained by the profound influence of the calcareous materials ($CaCO_3$) deposited (Eq. 3), and possibly, due to seawater intrusion into the Langat River (Connell and Miller 1984; Reza and Singh 2010).

$$H_2O + CaCO_3 \rightarrow Ca^{2+} + HCO_3^- + OH^-. \tag{3}$$

Redox potential (*Eh*) measured the ability of the aquatic system to supply electrons to an oxidizing agent or take up electrons from a reducing agent. The *Eh* value ranged from −17.60 to 150.60 mV, where the lowest value was observed in LY11 and highest in LY1. The perfect negative relationship between pH and *Eh* ($r = -1.000$, $p < 0.01$; Table 4) suggested that the *Eh* is strongly dependent on the changes in pH. The content of H^+ ions in natural water is mainly related to the quantitative ratio or carbonic acid and its ions. A high *Eh* value indicates an oxidation process in which water has a tendency to gain an electron such as H^+, between chemical species and become acidic while a low *Eh* value indicates high reduction (Radojević and Bashkin 2007).

The recorded temperatures for all stations were similar. This could be explained by the weather conditions (cloudy and drizzle) throughout the sampling period. Even though the temperature is not as significant as other parameters, it has a profound effect on DO. DO is positively correlated with temperature as illustrated in Table 4 ($r = 0.750$, $p < 0.01$, Table 4). The mean DO is 3.25 ± 1.14 mg/L. The increase in DO may be attributed to the higher photosynthetic rate accompanied by a higher light intensity on the surface waters (Wheeler et al. 2003). However, the

Table 3 Descriptive statistics for selected water matrices at Langat River ($n = 90$)

	Unit	Min	Max	Range	Mean ± SD	CV	WHO	MOH
pH	–	4.79	7.48	2.69	6.67 ± 0.53	7.95	6.5–9.2	6.5–9.0
Eh	mV	−17.60	150.60	168.20	32.95 ± 33.17	100.68	NA	NA
Temp	°C	26.80	29.90	3.10	28.27 ± 1.03	3.63	NA	NA
EC	mS/cm	0.09	37.40	37.32	14.55 ± 16.18	111.16	1.50	NA
Sal	ppt	0.05	23.70	23.65	9.07 ± 10.18	112.17	NA	NA
DO	mg/L	1.50	5.40	3.90	3.25 ± 1.14	35.18	NA	NA
TDS	mg/L	42.40	18,720.00	18,677.60	7,287.71 ± 8,101.91	111.17	NA	1,000
Na	mg/L	5.21	11,183.00	11,177.79	4,022.32 ± 4,543.16	112.95	200	200
Ca	mg/L	2.55	356.15	353.60	134.18 ± 151.52	112.92	200	NA
K	mg/L	0.56	171.95	171.39	47.68 ± 61.56	129.11	200	NA
Mg	mg/L	0.70	1,230.70	1230.00	452.24 ± 508.22	112.38	150	150
HCO_3	mg/L	9.76	139.08	129.32	61.92 ± 45.19	72.98	NA	NA
Cl	mg/L	10.00	8,347.41	8,337.41	3,001.39 ± 3409.88	113.61	250	NA
NO_3	mg/L	0.50	12.10	11.60	3.25 ± 2.97	91.22	50	NA
SO_4	mg/L	2.00	1,325.00	1,323.00	508.78 ± 570.22	112.08	250	250
Al	μg/L	1.15	5,191.70	5,190.56	290.07 ± 817.50	281.83	200	200
Ba	μg/L	<0.005	30.71	30.71	7.14 ± 7.32	102.57	700	700
Cd	μg/L	<0.01	0.53	0.53	0.11 ± 0.12	103.79	3	3
Cu	μg/L	0.57	81.02	80.45	28.16 ± 29.70	105.49	2,000	1,000
Fe	μg/L	81.79	807.15	725.36	312.60 ± 156.74	50.14	NA	300
Pb	μg/L	< 0.005	6.99	6.99	1.07 ± 1.64	153.25	10	10
Mn	μg/L	<0.005	640.07	640.07	87.14 ± 119.60	137.26	400	100
Zn	μg/L	0.95	65.06	64.11	15.21 ± 14.29	93.94	NA	3000
Co	μg/L	0.06	6.22	6.17	0.64 ± 1.14	180.15	NA	NA
Be	μg/L	<0.05	1.10	1.10	0.13 ± 0.23	176.29	NA	NA
Cr	μg/L	0.32	4.67	4.35	1.13 ± 0.91	80.03	50	50
Ni	μg/L	0.80	24.72	23.92	7.29 ± 6.75	92.56	20	20
Se	μg/L	<0.10	265.00	265.00	87.86 ± 101.31	115.31	10	20

Eh redox potential; *Temp* temperature; *EC* electrical conductivity; *Sal* salinity; *DO* dissolved oxygen; *TDS* total dissolved solids; *NA* not available

variation in DO values not only depends on climate condition but also on chemical, biological and microbiological processes (Yang et al. 2007). Yayintaş et al. (2007) stated that DO values less than 3 mg/L indicate the occurrence of water pollution. The presence of natural organic matter, waste discharge from domestic, agricultural and industrial effluent also depletes the DO content (Yang et al. 2007; Yayintaş et al. 2007). Lee et al. (2006) mentioned that the Langat River was under stress from pollution, particularly from domestic waste and industrial discharge. Therefore, the stations, which are located in close proximity to the major pollution sources, exhibited a lower DO value, which is attributed to the biological and microbiological processes.

The EC, TDS and salinity values ranged from 0.09 to 37.40 mS/cm, 42.40 to 18,720.00 mg/L and 0.05 to 23.70 ppt, respectively. About 47 % of the samples (LY1–LY14; downstream) exhibited an EC value greater than 1.50 mS/cm stipulated by WHO (2004) while 43 % of samples exhibited a TDS value greater than 1,000 mg/L recommended by MOH (2004). The EC measurement indicates the water's ability to conduct an electric current (Radojević and Bashkin 2007), and is largely dependent on the concentration of dissolved ions such as inorganic salt and organic matter in the water. The different values of EC represent the relative difference of ion constituent in water between each station. In addition, TDS is also considered to be a good indicator of the presence of dissolved ions, such as inorganic salt and organic matter in water (WHO 2004; Reza and Singh 2010). In general, the greater the amount of dissolved solids in the water, the greater is the water's conductivity. Hence, the EC of a water sample is proportional to the amount of dissolved solids, which is supported by the perfect positive correlation between the EC and TDS values ($r = 1.000$, $p < 0.01$; Table 4). Certain sampling stations were located comparatively nearer to

Table 4 Pearson correlation coefficient (*r*) between in situ parameters and major ions ($n = 90$)

	pH	*Eh*	TEMP	EC	SAL	DO	TDS	HCO_3	Cl	NO_3	SO_4	Na	Ca	K	Mg
pH	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
Eh	**−1.000**	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
TEMP	0.509	−0.505	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
EC	0.661	−0.660	**0.920**	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
SAL	0.669	−0.669	**0.918**	**1.000**	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
DO	0.472	−0.473	**0.750**	**0.774**	**0.780**	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
TDS	0.661	−0.660	**0.920**	**1.000**	**1.000**	**0.774**	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
HCO_3	**0.831**	**−0.831**	**0.825**	**0.930**	**0.933**	**0.708**	**0.930**	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
Cl	0.479	−0.478	**0.869**	**0.942**	**0.939**	**0.722**	**0.942**	**0.828**	1	0.000**	0.000**	0.000**	0.000**	0.000**	0.000**
NO_3	−0.382	0.383	−0.544	−0.642	−0.640	−0.538	−0.642	−0.597	−0.622	1	0.000**	0.000**	0.000**	0.000**	0.000**
SO_4	**0.767**	**−0.766**	**0.875**	**0.973**	**0.972**	**0.701**	**0.973**	**0.955**	**0.883**	−0.622	1	0.000**	0.000**	0.000**	0.000**
Na	0.548	−0.548	**0.905**	**0.967**	**0.961**	**0.686**	**0.967**	**0.868**	**0.947**	−0.643	**0.946**	1	0.000**	0.000**	0.000**
Ca	**0.773**	**−0.772**	**0.890**	**0.986**	**0.988**	**0.753**	**0.986**	**0.967**	**0.897**	−0.625	**0.986**	**0.931**	1	0.000**	0.000**
K	**0.703**	**−0.702**	**0.803**	**0.911**	**0.917**	**0.737**	**0.911**	**0.887**	**0.895**	−0.568	**0.880**	**0.823**	**0.926**	1	0.000**
Mg	0.590	−0.590	**0.907**	**0.973**	**0.968**	**0.689**	**0.973**	**0.886**	**0.939**	−0.643	**0.961**	**0.997**	**0.946**	**0.831**	1

The bold values are correlation value above 0.70 that taken

Significant value (upper triangle; ** $p < 0.01$, * $p < 0.05$; 2-tailed)

Correlation value (lower triangle)

the Strait of Malacca, which were easily affected by tidal movements and also the discharge regimes of river water. When tidal movements are stronger than the river discharge, seawater will penetrate into the river (Radojević and Bashkin 2007), and dissolved inorganic salt, such as halite (NaCl) from the ocean mixes with the river water. The dissolution or dissociation of halite from the ocean contributed more free ions into the river water and changed their chemical composition (Aris et al. 2012; Eq. 4). In addition, Aris et al. (2012) found that high values of EC (EC > 5,000 μS/cm) could be related to seawater intrusion, which usually leads to a wide salinity range as proven by the strong correlation between EC and salinity ($r = 1.000$, $p < 0.01$; Table 4).

$$\mathrm{NaCl} \overset{\mathrm{H_2O}}{\leftrightarrow} \mathrm{Na^+} + \mathrm{Cl^-}. \quad (4)$$

Ion concentrations and distribution

A trilinear plot (ternary diagram) illustrates the major ions constituents and the differences in water chemistry between stations. The ternary diagram shows that the cations were in the order of $Na^+ K > Mg > Ca$ while anions were in the order of $Cl > HCO_3 > SO_4^+ NO_3$ (Fig. 3). Na–Cl facies was dominant in most parts of the downstream section (LY1–LY14) of the study area and shifted to Ca–HCO_3 facies when moving upward (LY15–LY30) as shown in Fig. 1. It was deduced that the mixing of seawater with freshwater (river) is an influential hydrochemical process in the study area as certain of the sampling stations (downstream proximity) are closer to the coastal area. The mixing process between saline water and freshwater usually leads to a wide TDS range (Aris et al. 2009). Therefore, the high TDS value may be due to the contributions of Na, Mg, Cl, HCO_3 and SO_4 in the samples. In addition, these ions were positively and significantly correlated with TDS, as shown in Table 4.

Cations and anions

Cations (Ca, Mg, Na and K) constitute more than 30 % of total element content of the Earth's crust (Alloway 1995). Major ion concentrations were found to be significantly higher (ANOVA, $p < 0.05$) in the Langat River as the dominant constituents in river water. The concentration values of Na, Mg, Cl, and SO_4 were significantly higher compared to Ca, HCO_3, K and NO_3 (ANOVA, $p < 0.05$). The mean concentration of Na was 4,022.32 ± 4,543.16 mg/L with a wide variance ranged from 5.21 to 11,183.00 mg/L. High Na concentrations were detected at LY1–LY14, which exceeded the WHO and MOH limits of 200 mg/L. The highest concentration was observed at LY10, which is 56 times greater than the guidelines. The

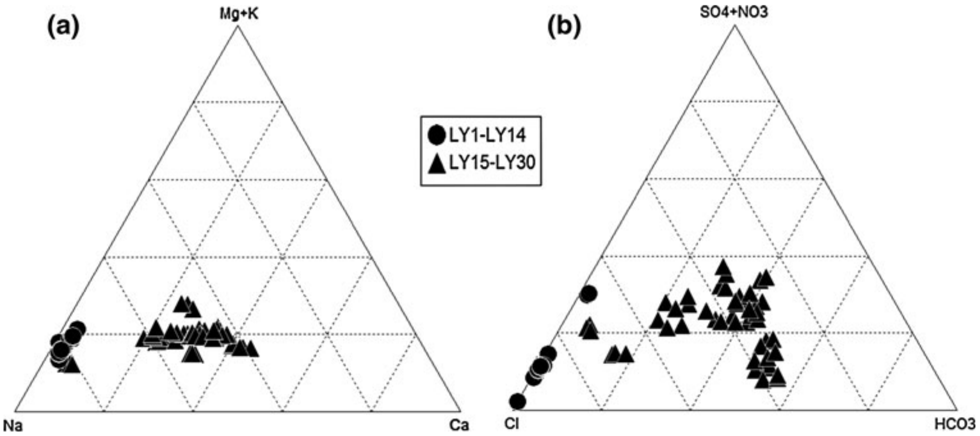

Fig. 3 Ternary plots for **a** cations and **b** anions of water samples in Langat River

elevated Na concentration might be due to the dissolution of minerals or mixing between seawater and freshwater. The high CV of Na (113 %) can be contributed to the influence from the mixing of seawater and freshwater observed in some locations. Na was highly correlated with Cl ($r = 0.947$, $p < 0.01$; Table 4), which indicated the influence of seawater on the salinity of the sample. The Na/Cl graph (Fig. 4) illustrated the possible mechanisms involved, such as weathering of silicate rocks, halite dissolution or ion exchange which contributed to the river-water constituents. The figure indicates that 59 % of the samples were greater than unity, which is explained by the silicate weathering, while 41 % of the samples were lower than unity, which is explained by the ion exchange process. The possible source of these excess ions is the intrusion of saline water, which was derived from the dissolution of inorganic salts from the ocean mixing with the river water according to the tide, and subsequently, leading to the ion exchange process (Appelo and Postma 2005; Eq. 5).

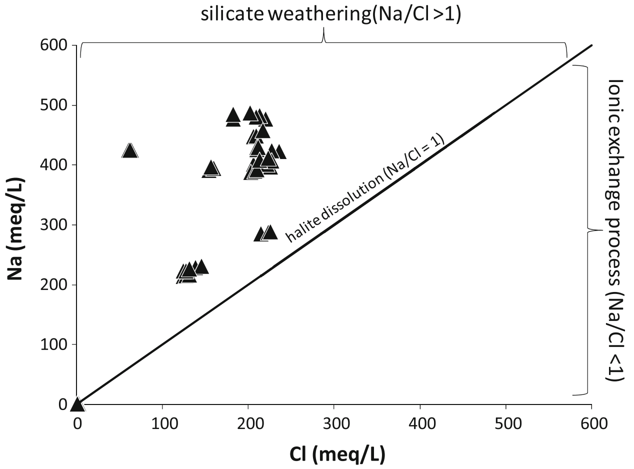

Fig. 4 Ion Na/Cl concentration to illustrate the ion exchange process

$$\mathrm{Na}^{+} + \frac{1}{2}\mathrm{Ca} - \mathrm{X}_2 \rightarrow \mathrm{Na} - \mathrm{X} + \frac{1}{2}\mathrm{Ca}^{2+} \qquad (5)$$

The dissolved concentration of Mg is higher than Ca and K. The Mg concentration ranged from 0.70 to 1,230.70 mg/L with an average value of 452.24 ± 508.22 mg/L. About 53 % of samples were well below the limits (150 mg/L) set up by WHO (2004) and MOH (2004). A positive and significant correlation between Mg and Cl ($r = 0.939$, $p < 0.01$; Table 4) suggests that a part of these dissolved ions may have been derived from marine sources. Another strong correlation was found between Mg and SO_4 ($r = 0.961$, $p < 0.01$; Table 4) and it was assumed that the Mg ions were attributed to the seawater. The Ca and K value ranged from 2.55 to 156.15 mg/L and from 0.56 to 171.95 mg/L, respectively. Under certain circumstances, Ca and K could be released through the weathering process. Usually the excess value of these variables has no direct impact on consumers but it will affect the taste of water and influences the users' acceptance of the water as being potable.

The concentrations of Cl and SO_4 ranged from 10.00 to 8,347.41 mg/L and 2.00 to 1,325.00 mg/L, respectively. Around 47 % of samples (LY1–LY14) exceeded the WHO and MOH limits (250 mg/L) for both ions. These two ions are considered major contributors to salinity in water and act as dominant anions in this study. The SO_4 concentration increased with NaCl concentration with strong correlations where it possessed Na ($r = 0.946$, $p < 0.01$; Table 4) and Cl ($r = 0.883$, $p < 0.01$; Table 4). The Cl ions are derived from dissolution of NaCl while SO_4 are either attributed to weathering of pyrite (FeS_2) or sulfate reduction. The collected water samples had the foul odor of rotten eggs indicating production of hydrogen sulfide (H_2S) by the sulfate-reduction process according to the mechanism below ($r = -0.766$, $p < 0.01$ for Eh and SO_4; Table 4; Eq. 6). This process also contributed to the concentration of HCO_3 with a strong positive relationship between HCO_3 and SO_4 ($r = 0.955$, $p < 0.01$; Table 4). This study also found a strong positive correlation between EC with

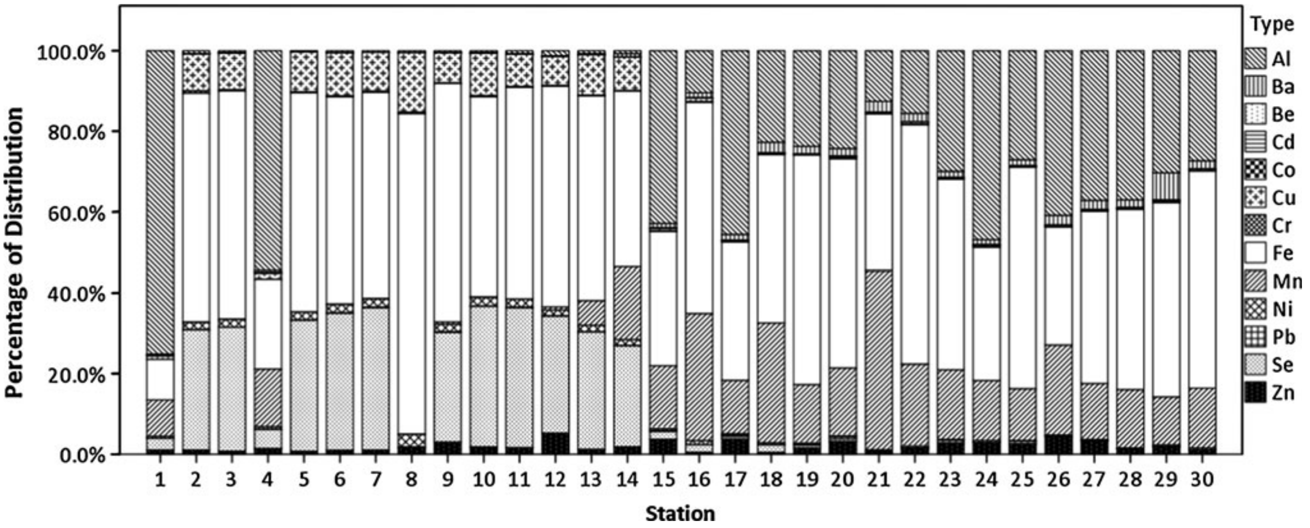

Fig. 5 Metal distribution according to sampling stations

salinity, TDS and major ions except for nitrate (Table 4), indicating the large contribution of these elements to the river water chemical load.

$$SO_4^{2-} + 2CH_2O \leftrightarrow 2HCO_3^- + H_2S. \quad (6)$$

Figure 5 illustrates the distribution of metals at each station. The order of metal distribution is as the follows: Fe > Al > Se > the rest of the measured metals. Fe and Al are the Earth's most abundant metallic elements with Al constituting about 8 % of the Earth's crust while Fe makes up at least 5 % of the Earth's crust (WHO 2004). The presence of Fe and Al may be due to geological weathering and also anthropogenic sources. In Malaysia, the soils are mainly acrisols, ferralsols, fluvisols, gleysols and others. Ferralsols (oxisols and ultisols) are rich in Al and Fe, acidic and highly weathered (Alloway 1995). Intense rainfall during the raining season will erode the topsoil, carrying with it high concentrations of Fe and Al by surface runoff. Hence, the elevated concentration of these metals observed in this study might be due to the weathering process. The concentration of Fe ranged from 81.79 µg/L to 807.15 µg/L with a mean value of 312.60 ± 156.74 µg/L. About 60 % of the collected sample exceeded the Malaysian National Standard for Drinking Water Quality (300 µg/L) (MOH 2004). Fe is not considered a hazard to health, since Fe is an essential nutrient for human consumption at a very minimal intake (WHO 2004). The water will have a metallic taste, will be reddish brown and have an offensive odor when the concentration exceeds 300 µg/L (MOH 2004; WHO 2004). Based on the visual inspection of the samples, all the samples were red. This may be due to the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) when exposed to the atmosphere (WHO 2004). The average concentration of Al ranged between 1.15 and 5,191.70 µg/L with an average value of 290.07 µg/L. The concentration of dissolved Al was low from LY2 to LY14 due to the relatively low solubility of natural Al minerals under neutral conditions or slightly alkaline condition (Radojević and Bashkin 2007; Fig. 5). Aluminium compounds such as aluminium oxide and aluminium hydroxide are insoluble in water except under extreme condition such as reduction of pH. Under acidic conditions, aluminium tends to dissociate into Al^{3+} in large amounts (WHO 2004; Eq. 7). The acidic condition at LY1 ($pH = 4.79$) and LY15–LY30 (pH ranged from 6.29 to 6.60) can cause an increase in the dissolved aluminium content in the surrounding waters. About 25 % of the samples collected in the Langat River exceeded the MOH (2004) and WHO (2004) permissible limits (200 µg/L). Exposure to Al has been hypothesized as a risk factor for the development or acceleration of the onset of Alzheimer's disease in humans once it exceeds the recommended daily uptake limit (WHO 2004).

$$2Al_2O_3 + 2OH^- \rightarrow AlO_2^- + H_2O. \quad (7)$$

The mean value of Se in Langat River is 87.86 ± 101.31 µg/L. The highest concentration was found at LY11 (251.67 ± 2.37 µg/L) whereas LY22–LY30 were below the limits of detection. The possible sources of Se may be attributed to the human activities and natural environment based on the geological characteristic of its station. The presence of Se can be attributed to several processes; in which the weathering of shales, which contain a substantial amount of Se and sulfide minerals could be possible sources attributed to natural origin. During weathering, such ore deposits can give rise to concentrations of dissolved trace elements. Se is often associated with heavy metal sulfides where it occurs as selenide (Se^{2-}), or as a substitute ion for sulfur in the crystal lattice (Adriano 2001). Electrolytic copper refining activities located

Table 5 Comparison of studied metals (μg/L) of river water in various river environments

	Al	Ba	Be	Cd	Co	Cu	Cr	Fe	Mn	Ni	Pb	Se	Zn
Present study	1.15–5,191.70	BDL–30.71	BDL–1.10	BDL–0.53	0.06–6.22	0.57–81.02	0.32–4.67	81.79–807.15	BDL–640.07	0.80–24.72	BDL–6.99	BDL–265.00	0.95–65.06
Langat River[a]	–	–	–	10–60	10–30	20–40	–	–	–	–	50–70	–	60–240
Terengganu River[b]	–	–	–	0.36–24.53	–	–	–	–	–	–	0.02–4.54	–	–
Mamut River[c]	–	–	–	0.13–0.83	2.02–4.04	10.60–17.10	0.27–3.33	5.36–22.40	368.00–472.00	21.70–33.80	1.03–4.83	–	10.10–45.20
Kipungit River[c]	–	–	–	0.11–0.35	BDL	0.42–6.20	BDL–0.52	2.33–5.48	0.10–1.24	0.50–1.98	BDL–2.14	–	2.86–9.39
Bebar River[d]	–	–	–	0.05–0.24	–	0.17–0.77	2.60–7.40	1270–1638	42–153	0.54–3.85	0.17–0.66	–	18.79–74.87
Skudai River[e]	–	–	–	0.10–2.63	–	2.99–168.57	3.42–60.81	–	–	1.47–212.44	0.93–16.69	–	21.06–125.18

BDL indicate value below detection limits

[a] Sarmani (1989)

[b] Sultan et al. (2011)

[c] Ali et al. (2004)

[d] Shuhaimi-Othman et al. (2009)

[e] Thanapalasingam (2005)

upstream might be from anthropogenic sources. About 70 % of the samples detected Se and 50 % of the samples exceeded the WHO (10 μg/L) and MOH limits (20 μg/L). Se is an essential element for humans, with a recommended daily intake of about 1 mg/kg of body weight for adults (WHO 2004).

The total concentrations of the studied metals in the river water were compared with those reported from this region and other studies in Malaysia (Table 5). The results were only compared with reliable analytical data that have been tested against metal spikes or standard reference materials (SRMs), rather than report based studies where analytical methods have not been described in detail. The results revealed that the metal concentrations in the Langat River were generally low and similar to those already reported in other Malaysian localities (Table 5). The wide range of certain metals indicated an occurrence of a point source input due to anthropogenic activities that are spatially distributed and controlled the spatial metals distribution in the study area. However, the comparative value analysis conducted in this study with the study of Sarmani (1989) showed evidence of improvement in the river water quality in Malaysia.

Hierarchical cluster analysis

Chemometric analysis, such as hierarchical cluster analysis (HCA), is a useful technique to investigate spatial and temporal variations (Singh et al. 2005; Praveena et al. 2011). HCA helps in grouping the objects (cases) into classes (clusters) on the basis of similarities within a class and dissimilarities between different classes from the dataset (Praveena et al. 2008, 2011). A picture of the group and their proximity with a dramatic reduction in dimensionality of the original data is illustrated by a dendrogram (Shrestha and Kazama 2007). In this study, the selected 28 variables were subjected to a HCA. Two main clusters (Group 1 and Group 2) were identified from 30 sampling stations (Fig. 6). Group 1 consisted of sampling stations LY1–LY14, which are in the proximity to the estuary and Strait of Malacca (Fig. 2). Based on the locations and variable concentrations at these stations, this study concluded that seawater intrusion strongly affects the south and south western parts of the study area. The common signatures of these stations were high in salinity, EC, and TDS values compared to the other stations. The movement of seawater towards the Langat River contributed to the high load of salinity, EC, and also additional ions, such as K, Mg and Na, to the downstream. Group 2 consisted of sampling station LY15–LY30, which are mainly located in the eastern part of the study area. In this area, the population density is considerably high and the land-use pattern is of predominantly urban activities and agricultural fields

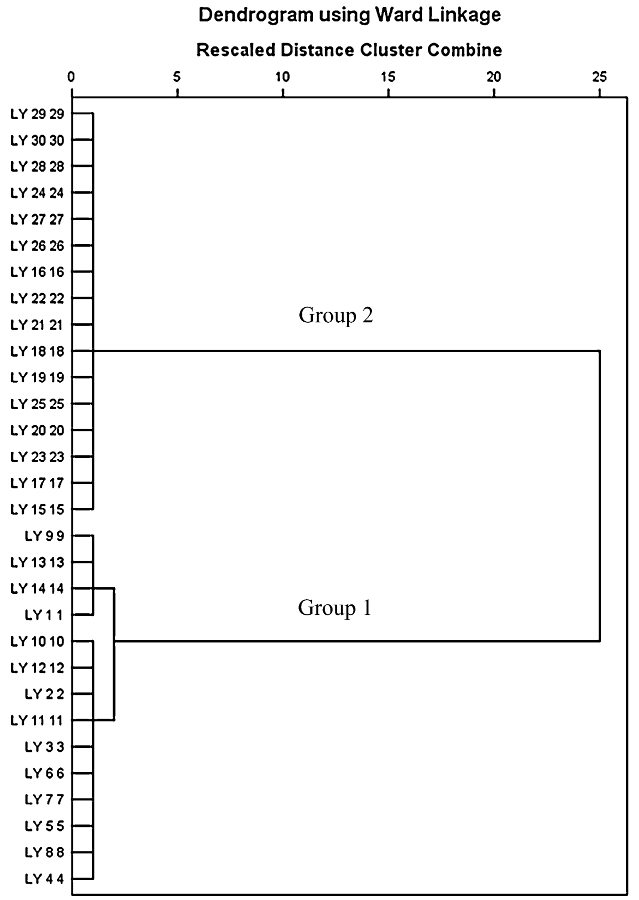

Fig. 6 Dendrogram showing hierarchical cluster analysis between stations

(DOA 1995; JICA and MGDM 2002; Fig. 2). Group 2 is associated with agricultural and industrial pollution. It is noteworthy that these are the sites that are susceptible to ecotoxicological impact. The sampling stations are mainly located further inland from the estuary and in close proximity to the major pollution sources, such as industrial discharge, domestic sewage from treatment plants, construction projects and pig farming. The HCA result is ratified by the land-use pattern of the basin (Fig. 2). In addition, Group 2 has less impact from seawater intrusion as compared to Group 1. The differences between Group 1 and Group 2 were also proven by the changing of water type from Na–Cl facies (LY1–LY14) to Ca–HCO_3 facies (LY15–LY30), as mentioned above.

Conclusions

This study highlights the potential substantial effect on the drinking purposes, especially at the downstream of the basin. For assessing the water quality using physico-chemical parameters, it was seen that stations located downstream and near estuaries (LY1–LY14) tend to have a higher range value than upstream (LY15–LY30) with 47 % of EC and 43 % of TDS values in samples exceeding the WHO and MOH standards. The average concentration for Al, Fe and Se were found to be higher than the recommended permissible value of WHO and MOH. This study shows that the hydrochemistry of the study area could be differentiated into two different types of water chemistry. These variances may be attributed to the hydrogeological factors, such as the weathering process and ion exchange process, apart from the anthropogenic sources, such as domestic and industrial waste loadings. The findings from this study will provide useful information concerning the hydrochemical variation and processes in the Langat River. The present study observed that the land-use activities exerted substantial influence on the hydrochemistry of the Langat River. The findings are useful in providing reliable classification of the stations in the study area and assist in identifying the priorities for sustainable river management.

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