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Assessment of water quality of man-made lakes in Klang Valley (Malaysia) using chemometrics: the impact of mining

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ABSTRACT

Assessing water quality of the ex-mining ponds for its proper utilization is pertinent considering the metal pollutants and lack of proper environmental measures is associated with the mining operations. In this study, water samples from 13 man-made lakes including 8 ex-mining ponds in the Klang Valley, Malaysia were analyzed for dissolved oxygen, suspended solid, pH, electrical conductivity (EC), biological oxygen demand (BOD), ammoniacal nitrogen (AN), total dissolved solid (TDS), and metals including As, Cd, Pb, Mn, Fe, Na, Mg, and Ca. The variations in these parameters were evaluated with the chemometric techniques. The results from the principal component analysis and hierarchical cluster analysis suggested that in addition to the degree of contamination, the variations in heavy metal concentrations were mainly attributed to the ex-mining activities, whereas deviations in BOD, TDS, AN, and EC were subjected to the current domestic inputs. The linear discriminant analysis showed that water samples from the ex-mining ponds were highly associated with Mn, Cd, Ca, and As. The As and Cd levels recorded in most of the ex-mining ponds were 11.3 ± 0.4, 116 ± 2, and 42 ± 0.5 μg/L; and 12.9 ± 0.2, 12.23 ± 0.02, 12.19 ± 0.01, and 12.15 ± 0.01 μg/L, respectively. These values surpassed the reference limits, which make them unfit for domestic uses.

Keywords: Chemometric; Ex-mining; Lake; Metal; Water

1. Introduction

There is an increasing demand for potable water supply in developing countries, thereby making water quality assessment and rating a pertinent subject in recent times [1]. Water is needed for drinking, hygiene, agriculture, and industrial activities, and with a growing world population, the need is increasing substantially [2]. The quality of surface water is principally influenced by both natural and human activities [3]. Among the anthropogenic activities is mining, which contributes to the economic development of some countries like Malaysia.

Besides the economic benefit of mining, there are numerous environmental hazards related to the course of exploration and extraction processes, resulting in the pollution of water, soil, and air [4]. After the completion of the mining operation, the mines were abandoned with no existing environmental protection program. The abandoned mines were not drained, mixed with surface water, and contaminate the underground water. The impact of pollution on the surface water in the mine area differs significantly when compared with other types of industrial pollution, especially in its potential to last at elevated levels for centuries or even millennia after the closure of the mine [5,6].

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Most minerals are quite stable before the mining process, but when mining commences, the minerals are exposed to weathering by the oxidation process, with the effects of atmospheric oxygen and water. The most common minerals are the sulphides such as arsenopyrite (FeAsS), galena (PbS), greenockite (CdS), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and millerite (NiS), and release the sulphate (SO_4^{2-}) and their constituents metal ions (Pb^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, and Fe^{2+}) and metalloid As into aqueous solution [6,7]. Mine tailings consist of finely ground rock particles rich in metals and residual chemicals used in the mining operation [8]. Consequently, tailings may drain away the metals for hundreds of years after the mining operation has stopped [9]. Thus, the metal concentrations in water are good indicators of the degree of contamination [10]. Furthermore, another crucial source of contamination is the acid solution generated during the oxidation of sulphur-containing minerals [11], sulphuric acid and sulphate of iron, which are obtained in the presence of thiooxidans or ferrooxidans thiobacillus bacteria [12,13]. As a result of low pH values, there exist additional mineral dissolution and subsequent release of toxic metals [14]. Even at high pH, the quality of water from the ex-mining ponds become degraded through the dissolution of contaminants, human activities, and concentration due to evaporation [15]. The concentrations of the metal pollutants are also considerably influenced by seasonal inconsistency [16,17].

Legislations on the mining code of practice were enacted in 1895 and reviewed in the subsequent years but did not specifically discuss environmental issues. The mining enactment of 1934 was the first law introduced to monitor the environmental standards and regulations during the mining operation. It requires mining companies to conduct rehabilitation of the excavated land to preserve the ecosystem and minimize pollution [18]. The pollution of soil, surface, and underground water was reported in some mining areas; As concentration was detected in the well water near the former tin-mining area in Malaysia where three cases of cutaneous lesions, which were related to arsenical poisoning, were discovered. As was found to co-exist with tin ore in the mining areas [19]. The exposure levels of some heavy metals especially Cd was found to be below what was previously expected [20].

The ex-mining ponds are now a major issue of concern, resulting in media hype and arguments on the intended use of such retention as an alternative source for human consumption and other domestic needs after conventional water treatment processes in the Selangor state [21]. However, the safety of the water from the ex-mining ponds is still not certified; only a few studies were carried out that did not have enough evidence to conclude on the quality status. This brings about the need to study, analyze, and compare the presence of toxic heavy metals and variations in the levels and concentrations of general water quality parameters in the ex-mining ponds and lakes that had no history of the mining operation. Thus, the objectives of this study were: (1) to assess and compare the concentrations of heavy metals and other physicochemical parameters in the water from ex-mining ponds and other man-made lakes; (2) to identify the most significant parameter(s) responsible for the variation in the quality of the water from those man-made lakes; and (3) to assess the quality of water of ex-mining ponds with a view to utilize them as an alternative source of water for human consumption and/or beneficial purposes.

Due to the fact that water from the ex-mining ponds is related to various geological and environmental states, multivariate analysis methods were applied to differentiate the samples. The chemometric techniques employed were the principal component analysis (PCA), hierarchical cluster analysis (HCA), and discriminant analysis (DA). These techniques have been used in both surface water and groundwater studies [22–24], including determining the sources and distribution of the pollutants [4,25], and water quality assessment of the ex-mining lakes and rivers [26–28]. The chemometric tools applied enable the identification of possible factors that influence the quality of water [29]. In this study, HCA, PCA, and DA were used to analyze the data and deduce on the multivariate differences and similarities among water quality variables, and identify particular variables responsible for the variation in lakes and ex-mining ponds.

2. Materials and methods

2.1. Study area

The Klang Valley (2.6817° N, 101.6613° E) is an area in central Selangor, centred in Kuala Lumpur, and its connecting cities (Fig. 1). Demarcated between the Mountains of Titiwangsa to the north and east, and to the west by the Strait of Malacca, Klang Valley is the central industrial and commercial region of Malaysia. It has a population of about 7.5 million people (about a quarter of Malaysian total population). The climate of the Klang valley is tropical rainforest that is warm with sunshine. There is abundant rainfall especially between October and March, with an average annual rainfall of 2,000–3,000 mm. The highest temperature in the study area is between 29°C and 32°C, with average humidity of 65%–70% except in June, July, and September usually considered as dry season with low rainfall [30,31]. The geology of the study sites varied with different rock types, but mostly dominated by Kenny hill formation especially in Puchong area with most of the ex-mining ponds; also the deposit of lime stone basement is predominant around Kuala Lumpur [32]. Most of Malaysian ex-mining ponds are located in the Selangor state due to the intensive mining activity with about 4,909.6 ha of ex-mining land. The ex-mining ponds are either abandoned, used for recreational activity, as flood retention, or to receive domestic effluents in the residential areas. Several cases of pollution were reported by the immediate residents including death of aquatic organisms in Kelana Jaya [33]. Also located in the study area were man-made lakes that had no previous mining activity (Table 1).

2.2. Sampling and field works

Water samples were collected from 13 man-made lakes (including 8 ex-mining ponds) in the Klang Valley (Table 1). Sampling was carried out from the 13 sites in the month of September 2015, which is the end of a period considered to have low level of rainfall. The samples were collected from 25 cm in depth using a Wildco vertical water sampler with three samples per sites, and the samples were replicated for analysis [34]. All samples were acidified with HNO_3 (Merck suprapur®) to lower the pH < 2 so as to prevent sedimentation of the metals [35], stored in the acid washed

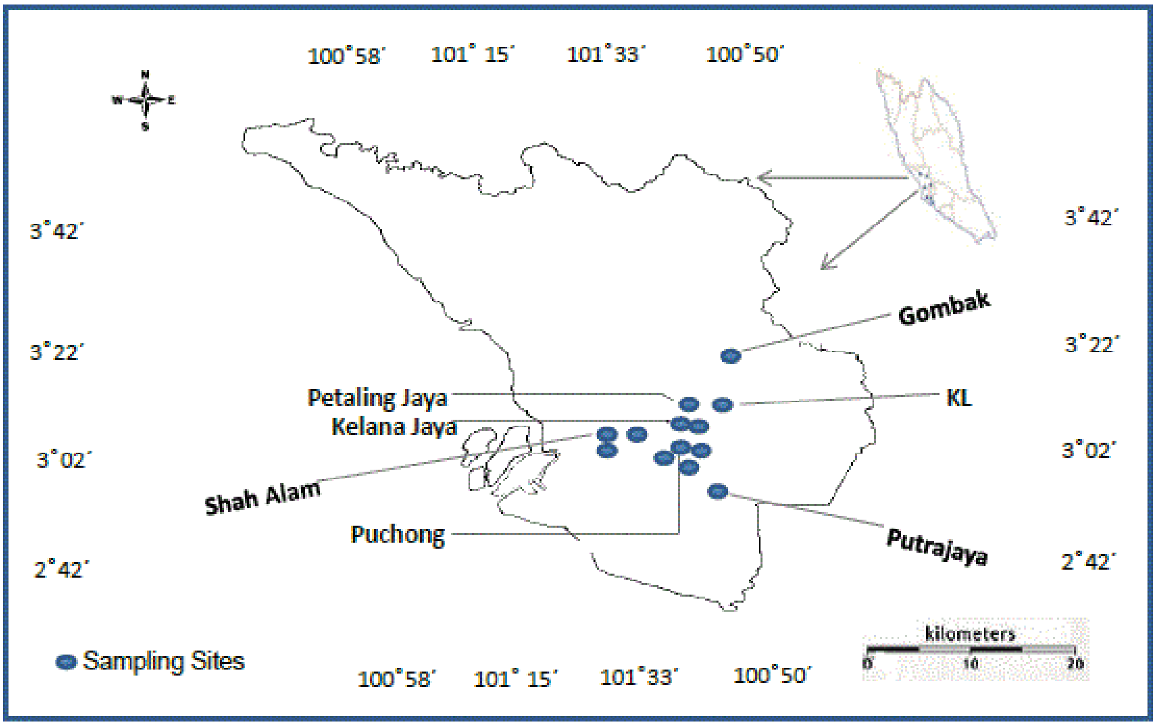

Fig. 1. Map of Malaysia showing sampling sites in Klang Valley, Selangor.

Table 1
Sampling sites

Type	Area	Sites	Code	Location	Uses
Ex-mining Ponds	Kelana Jaya	Tasik Kelana Jaya	TKJA	N 03°05′35.4″–E 101°35′53.2″	Recreational, flood retention, domestic effluent
			TKJB	N 03°05′57.1″–E 101°35′40.9″	
	Gombak	Tasik Biru	TB	N 03°14′50.9″–E 101°31′38.6″	Recreational
	Puchong	Tasik Saujana Putra	TSP	N 02°56′50.4″–E 101°34′37.2″	Recreational
		Tasik Putra Perdana	TPPA	N 02°57′27.8″–E 101°36′52.2″	Recreational
			TPPB	N 02°57′46.4″–E 101°36′21.8″	
		Tasik Prima Perdana	TPRP	N 02°59′10.0″–E 101°35′49.4″	Recreational, water sports
	Titiwangsa	Tasik Titiwangsa	TT	N 03°10′35.3″–E 101°42′21.3″	Recreational, water sports
Other man-made lakes	Petaling Jaya	Tasik Taman Jaya	TTJA	N 03°06′17.8″–E 101°38′53.0″	Recreational, residential waste
	Kuala Lumpur	Tasik Perdana	TP	N 03°08′31.9″–E 101°41′06.5″	Recreational
	Shah Alam	Tasik Shah Alam	TSA	N 03°04′27.0″–E 101°30′47.3″	Recreational
		Tasik Shah Alam 7	TS7	N 03°04′42.4″–E 101°29′28.7″	Recreational, domestic effluent
	Putrajaya	Tasik Putrajaya	TPJ	N 02°55′12.5″–E 101°40′52.6″	Recreational, water sports

polyethylene bottles and transported to laboratory in ice boxes conserved at 4°C for metal analysis. Other parameters like dissolved oxygen (DO), pH, electrical conductivity (EC), total dissolved solid (TDS), and ammoniacal nitrogen (AN) were measured and recorded in the field using portable YSI Pro Multiparameter Water Quality Meter (professional series), and the total suspended solid (TSS) was measured using the DR900 suspended solid meter. The biological oxygen demand (BOD) was also measured in-situ using a water portable meter (s/no. 005) to avoid changes in the bacterial concentration with time.

2.3. Heavy metal analysis

The triplicates of each water sample were filtered using the 0.45-µm polytetrafluoroethylene filters prior to the inductively coupled plasma-mass spectrophotometry (ICP-MS). The filtered water samples were then analyzed for As, Cd, Pb, Mn, Fe, Na, Mg, Ca, Cr, V, Cu, Zn, Th, and Tl with ICP-MS 7500ce (Agilent Scientific Technology Ltd., USA) [36,37]. The sample injection system was made up of a nebulizer and temperature controlled spray chamber attached to an auto-sampler. In order to maintain the sensitivity of the instrument, the operating conditions (Table 2) were tuned on daily basis with a tuning mixture consists of 10 mg/L Ce, Co, Tl, Li, and Y in 0.5% HCl and 2% HNO_3 [38]. The concentrations of Cr, V, Cu, Zn, Th, and Tl in most of the water samples analyzed were below the detection limit and, therefore, not further considered.

2.4. Quality control in ICP-MS analysis

Quality control (QC) and quality assurance were practiced to assure the reliability of the results. All the plastic wares used were soaked in 15% HNO_3 (v/v) and rinsed twice with ultrapure water (UPW) produced from PURELAB® UHQ II system (ELGA®, UK). In the preparation of blanks and standard solutions, UPW was used. The multielemental calibration stock solution of 1,000 mg/L for Fe, Na, Ca, and Mg and 10 mg/L for As, Cd, Pb, Mn, Zn, V, Cr, U, Th, and Tl (Agilent Technologies, Newcastle) was used to prepare the calibration and QC solutions by appropriate dilution. Certipur® reference materials for ICP (Merck, Germany) and SLR-4 riverine water reference material for trace metals (National Research Council of Canada) were used to verify the ICP-MS procedure. Blank and QC samples were checked after every 10 samples to demonstrate the validity of the previous runs. All analyses were carried out in triplicate, and the results were expressed as the 95% confidence interval of the mean in μg/L.

Table 2
Instrumental and operating conditions for ICP-MS 7500ce

Power (W)	1,550
Plasma gas flow rate (L/min)	15
Auxiliary gas flow rate (L/min)	0.75
Sample depth (mm)	6–8
Carrier gas flow (L/min)	0.8–1.3
Sampler and skimmer cone	Ni
He or H_2 gas flow (L/min)	3–5

2.5. Data analysis

For the water quality data set obtained, the descriptive statistics were determined (mean, minimum, and maximum values). For the non-detected concentrations, the detection limit of the metals was adopted [39]. The calculations were carried out using MS Excel 2013, and one way ANOVA was applied to study the difference among the sampling stations. The statements reported in this study are at $p < 0.05$ levels.

Multivariate statistical analysis was carried out using JMP Pro 12. The pattern recognition techniques including PCA, HCA, and linear discriminant analysis (LDA) were used to explore the data matrix (117 × 15) of eight metals and seven water quality parameters. For LDA, 81/117 of the data set was randomly selected for training, and the remaining 36/117 for validation [40]. The standardized sets of data of the variables were used for PCA to reduce the influence of different variables, and ignore any dominance of large size variables in the data set. HCA was performed on the data set using the Ward's method (with Euclidean distance) as the measure of similarity and difference [41,42]. In LDA, a discriminant function was computed using the eigenvalues to predict the group identity of a sample [43].

3. Results and discussion

3.1. ICP-MS method verification

The coefficient of determinant (R^2) for ICP-MS calibration curves was >0.999. The measurement results (Table 3) demonstrated a good agreement with the certified values with recoveries ranging between 88% and 107%. This is comparable with the analytical performance reported in a similar study [44].

3.2. The variations in metals concentrations

Tables 4 and 5 present the means, standard deviations, and ranges of the 15 water quality variables and their permissible levels. Among the parameters, heavy metals are

Table 3
ICP-MS measurements on certified reference material

Isotope of analyte		^{75}As	^{111}Cd	^{208}Pb	^{55}Mn	^{56}Fe	^{23}Na	^{24}Mg	^{43}Ca
Analysis mode		He	Normal	Normal	He	H_2	Normal	Normal	Normal
Detection limit (μg/L)		0.1	0.004	0.05	0.03	2	1.27	0.3	1.18
Certipur® reference material for ICP	Certified (μg/L)	50 ± 5	20 ± 5	25 ± 5	30 ± 5	100 ± 10	(8.0 ± 0.5) × 10^3	(1.50 ± 0.05) × 10^4	(3.5 ± 0.1) × 10^4
	Measured (μg/L)	46 ± 1	19 ± 1	27 ± 2	29 ± 1	105 ± 5	(8.3 ± 0.9) × 10^3	(1.55 ± 0.05) × 10^4	(3.6 ± 0.1) × 10^4
	Recovery (%)	92 ± 1	97 ± 4	106 ± 17	98 ± 8	107 ± 12	102 ± 4	101 ± 1	104 ± 7
SLRS-4	Certified (μg/L)	0.68 ± 0.06	0.012 ± 0.002	0.086 ± 0.007	3.37 ± 0.18	103 ± 5	2.4 ± 0.2	1.6 ± 0.1	6.2 ± 0.2
	Measured (μg/L)	0.59 ± 0.011	0.011 ± 0.001	0.081 ± 0.003	3.36 ± 0.03	108 ± 3	2.5 ± 0.2	1.5 ± 0.2	6.7 ± 0.3
	Recovery (%)	88 ± 5	98 ± 9	94 ± 4	99 ± 3	105 ± 6	101 ± 8	97 ± 7	106 ± 5

Table 4
Descriptive statistics of water quality parameters on ex-mining ponds in Klang Valley

Variable	TKJA	TKJB	TB	TSP	TPPA	TPPB	TPRP	TT
As	7.5 ± 0.2 (7.0–7.8)	6.8 ± 0.3 (6.4–7.1)	0.53 ± 0.02 (0.50–0.56)	0.67 ± 0.03 (0.62–0.75)	11.3 ± 0.4 (10.9–11.9)	116 ± 2 (114–118)	42.0 ± 0.5 (41.4–42.6)	2.13 ± 0.05 (2.05–2.22)
Cd	0.03 ± 0.01 (0.02–0.04)	0.09 ± 0.01 (0.08–0.10)	0.01 ± 0.01 (0.01 -0.02)	1.14 ± 0.02 (1.11 -1.19)	12.9 ± 0.2 (12.7–13.2)	12.23 ± 0.02 (12.20–12.28)	12.19 ± 0.01 (12.19–12.20)	12.15 ± 0.01 (12.14–12.19)
Pb	0.23 ± 0.03 (0.20–0.26)	0.79 ± 0.06 (0.72–0.87)	<0.05	13.5 ± 0.1 (13.3–13.8)	4.5 ± 0.3 (4.1–4.9)	3.6 ± 0.2 (3.4–3.9)	3.7 ± 0.3 (3.3–4.0)	3.51 ± 0.07 (3.43–3.62)
Mn	124 ± 3 (120–130)	36.4 ± 0.8 (35.2–37.3)	18.0 ± 0.6 (17.0–18.8)	438 ± 2 (435–440)	125 ± 2 (123–128)	1.4 ± 0.3 (1.0–1.78)	3.3 ± 0.1 (3.1–3.4)	11.4 ± 0.2 (11.2–11.7)
Fe	1,166 ± 11 (1,146–1,185)	241 ± 1 (239–243)	240 ± 2 (237–244)	360 ± 5 (353–369)	460 ± 4 (455–470)	35.8 ± 0.6 (35.1–36.8)	15.1 ± 0.1 (14.9–15.4)	34 ± 2 (31–40)
Na	8,093 ± 69 (7,932–8,197)	17,247 ± 199 (16,935–17,495)	4,303 ± 34 (4,228–4,339)	3,876 ± 43 (3,810–3,955)	14,516 ± 153 (14,225–14,785)	12,367 ± 205 (12,115 -12,705)	10,572 ± 68 (10,445–10,695)	1,484 ± 7 (1,474–1,494)
Mg	1,554 ± 20 (1,523–1,589)	1,561 ± 27 (1,509–1,591)	718 ± 6 (710–725)	4,903 ± 40 (4,816–4,949)	2,219 ± 106 (2,061–2,330)	1,853 ± 32 (1,815–1,914)	3,863 ± 23 (3,830–3,904)	5,628 ± 25 (5,595–5,684)
Ca	23,513 ± 374 (23,054–24,463)	28,545 ± 326 (28,014–28,944)	12,500 ± 336 (12,084–12,904)	25,428 ± 256 (24,974–25,704)	21,277 ± 161 (20,994–21,474)	34,246 ± 179 (34,034–34,614)	44,346 ± 454 (43,244–44,944)	27,632 ± 256 (27,294–28,014)
DO	0.91 ± 0.07 (0.84–1.00)	1.35 ± 0.07 (1.26–1.41)	4.2 ± 0.1 (4.1–4.4)	5.2 ± 0.2 (5.0–5.3)	6.1 ± 0.1 (6.0–6.3)	0.38 ± 0.03 (0.36–0.42)	0.47 ± 0.04 (0.42–0.51)	4.11 ± 0.09 (4.00–4.21)
BOD	5.9 ± 0.4 (5.1–6.2)	9.7 ± 0.1 (9.6–9.9)	2.5 ± 0.2 (2.2–2.7)	3.4 ± 0.8 (2.4–4.4)	8 ± 1 (6–9)	2.8 ± 0.3 (2.4–3.1)	2.77 ± 0.07 (2.70–2.87)	1.5 ± 0.1 (1.4–1.7)
TDS	89 ± 1 (87–91)	125 ± 1 (124–126)	46 ± 1 (45–47)	172 ± 1 (170–174)	132 ± 1 (131–133)	161 ± 1 (160–162)	161 ± 1 (160–161)	113 ± 2 (111–115)
pH	0.93 ± 0.09 (0.84–1.10)	1.35 ± 0.06 (1.26–1.40)	4.2 ± 0.2 (4.1–4.4)	5.2 ± 0.1 (5.0 -5.3)	6.1 ± 0.2 (5.9–6.3)	10.00 ± 0.09 (9.87–10.09)	8.23 ± 0.09 (8.10–8.33)	8.25 ± 0.05 (8.20–8.32)
TSS	4.6 ± 0.5 (4.0 -5.0)	16 ± 1 (15–18)	<5	<5	6.7 ± 0.5 (6.0–7.0)	<5	<5	< 5
AN	0.16 ± 0.02 (0.13–0.19)	0.33 ± 0.01 (0.31–0.34)	0.06 ± 0.01 (0.05–0.07)	0.09 ± 0.01 (0.08–0.09)	0.25 ± 0.03 (0.22–0.28)	0.16 ± 0.01 (0.15–0.18)	0.19 ± 0.01 (0.18–0.21)	0.05 ± 0.01 (0.04–0.06)
EC	145 ± 2 (142–146)	203 ± 1 (202–204)	75 ± 1 (73–77)	286 ± 2 (284–288)	217 ± 2 (215–219)	276 ± 1 (274–278)	281 ± 1 (280–282)	189 ± 1 (187–190)

Note: All parameters are presented in mg/L except for metal concentrations, electrical conductivity and pH, which are given in μg/L, μs/cm, and no unit, respectively.

Table 5
Descriptive statistics of water quality parameters on other man-made lakes and RWQC values

Variable	TTJA	TP	TSA	TS7	TPJ	DWQSRW	INWQS-Class IIA
As	1.13 ± 0.06 (1.03–1.21)	3.8 ± 0.1 (3.7–4.0)	3.37 ± 0.2 (3.03–3.58)	14.4 ± 0.4 (13.9–14.9)	7.5 ± 0.3 (6.9–7.9)	10	50
Cd	0.33 ± 0.02 (0.30–0.37)	0.06 ± 0.01 (0.05–0.07)	0.02 ± 0.01 (0.02–0.03)	0.05 ± 0.01 (0.05–0.06)	12.17 ± 0.01 (12.17–12.18)	3	10
Pb	0.52 ± 0.02 (0.49–0.56)	0.36 ± 0.01 (0.34–0.38)	<0.05	0.66 ± 0.02 (0.63–0.70)	4.4 ± 0.2 (4.1–4.6)	50	–
Mn	186 ± 1 (185–190)	35.7 ± 0.3 (35.3–36.4)	68 ± 2 (64–70)	405 ± 3 (398–411)	100 ± 1 (99–101)	200	100
Fe	151 ± 4 (144–158)	228 ± 6 (215–237)	279 ± 6 (266–290)	1,540 ± 25 (1,485–1,575)	841 ± 7 (825–848)	1 000	1 000
Na	5,269 ± 34 (5,216–5,304)	3,320 ± 37 (3,255–3,375)	5,540 ± 44 (5,472–5,594)	9,870 ± 25 (9,843–9,906)	21,520 ± 276 (21,025–21,995)	200 000	–
Mg	1,829 ± 16 (1,807–1,863)	2,234 ± 40 (2,180–2,299)	2,716 ± 46 (2,614–2,793)	3,043 ± 30 (3,002–3,104)	1,650 ± 21 (1,608–1,678)	150 000	–
Ca	15,280 ± 73 (15,214–15,464)	25,194 ± 57 (25,104–25,274)	43,423 ± 184 (43,104–43,654)	21,256 ± 70 (21,134–21,364)	31,245 ± 128 (30,914–31,394)	–	–
DO	3.3 ± 0.2 (3.1–3.5)	3.6 ± 0.1 (3.5–3.8)	2.8 ± 0.1 (2.6–2.9)	1.33 ± 0.05 (1.27–1.38)	4.4 ± 0.1 (4.2–4.5)	–	5–7
BOD	7.5 ± 0.2 (7.2–7.6)	3.54 ± 0.07 (3.47–3.63)	8.85 ± 0.08 (8.76–8.96)	8.2 ± 0.2 (7.9–8.5)	2.10 ± 0.09 (1.98–2.21)	6	3
TDS	176 ± 2 (174–178)	87 ± 2 (85–90)	109 ± 1 (108–110)	117 ± 2 (115–120)	90 ± 2 (88–92)	1,500	1,000
pH	7.9 ± 0.2 (7.6–8.0)	8.32 ± 0.02 (8.29–8.35)	8.49 ± 0.03 (8.47–8.51)	7.6 ± 0.1 (7.4–7.8)	8.5 ± 0.1 (8.4–8.7)	5.5–9.0	6–9
TSS	9.7 ± 0.5 (9.0–10.0)	6.7 ± 0.9 (6.0–8.0)	13.7 ± 0.5 (13.0–14.0)	<5	<5	–	50
AN	0.33 ± 0.02 (0.31–0.36)	0.23 ± 0.02 (0.20–0.25)	0.02 ± 0.01 (0.02–0.03)	0.49 ± 0.05 (0.44–0.55)	0.16 ± 0.01 (0.15–0.18)	–	0.3
EC	291 ± 1 (290–292)	147 ± 1 (146–148)	184 ± 1 (182–185)	205 ± 3 (201–208)	146 ± 2 (144–148)	–	1,000

Note: All parameters are presented in mg/L except for metal concentrations, electrical conductivity, and pH which are given in μg/L, μs/cm, and no unit, respectively. DWQSRW – Drinking Water Quality Standard for Raw Water [53] and INWQS – Interim National Water Quality Standards for Malaysia [52].

of much concern in water researches due to their ability to deteriorate the aquatic ecosystem, bio-accumulate and an increase in the concentrations of the toxic levels rendering water unsuitable for human consumption, irrigation, and recreational activities [45,46]. The concentrations of the metals varied significantly ($p < 0.05$) with As, 0.50–118.36 μg/L; Cd, 0.10–13.18 μg/L; Pb, <0.05–13.77 μg/L; Mn, 1.02–440.71 μg/L; Fe, 15–1,185 μg/L; Na, 3,810–17,495 μg/L; Mg, 710–4,949 μg/L; and Ca, 12,084–44,944 μg/L. Such variation could be originated from the variability inherited from the mining activity, historical background of the ex-mining ponds, and additional variations by the ongoing anthropogenic inputs. The ore commonly mined in Selangor is tin from mineral cassiterite as tin oxide (SnO_2). The metals associated with tin ore are As, Cd, Pb, and Zn, and usually released to the environment by dissolution and erosion [47,48]. As, Cd, Pb, Mn, Fe, and Ni were found in the mining area and related to the ores and rocks crushed during the mining process [49]. However, most variations in the heavy metal concentrations were usually due to the percentage natural abundance, natural precipitation and aeration, and dilution factor due to water from external sources [50].

As is one of the heavy metals of concern, and it is a threat to the environment due to its poisonous nature. Cd is naturally found in small quantities in water, soil, and air [51], and it is a toxic element not required by plants. Based on the Interim National Water Quality Standards for Malaysia (INWQS), the mean concentrations of both elements in all the samples were below the benchmark level for Class IIA water supplies (which require conventional treatment before use) [52]; when referring to the Drinking Water Quality Standard for Raw Water (DWQSRW), As and Cd concentrations in Tasik Putra (TPPA), Perdana (TPPB), and Tasik Prima Perdana (TPRP), As concentration in Tasik Shah Alam 7 (TS7) and Cd concentrations in TPJ and TT were higher than the recommended values of 10 and 3 μg/L, respectively [53]. High As and Cd were detected in TPPA, TPPB, and TPRP located in Puchong, which is an area that had active and extensive mining activities [18]. Similarly, a high concentration of As (66 mg/L) had been reported in the Bestari Jaya ex-mining ponds [10], and traces of Cd (0.04 mg/L) in the Kelana Jaya ex-mining ponds. These results suggested that relatively high metal concentrations of As and Cd are plausibly related to the ex-mining activities [54,55]. Conversely, TS7 (a non-ex-mining lake) was also found to have a high As concentration. This can be related to the urbanization and densely industrialization in Shah Alam area, where the sources of As include industrial burning of fossil fuel, agrochemical, and steel and metal coating industries [18,56]. Similarly, it appears that the source of high Cd concentrations in TPJ could be due to the frequent national and international water sports competitions, transport, and other recreational activities.

Pb is accounted for 13 mg/kg of the earth crust [49]. In this study, the Pb concentrations found in all cases were below DWQSRW requirement of 50 μg/L and were even below the method detection limit (0.05 μg/L) for Tasik Biru (TB) and Tasik Shah Alam (TSA). Pb concentrations in the range of 19–75 μg/L were reported in the ex-mining ponds of Perak [57]. Mn concentrations in TS7 and Tasik Saujana Putra (TSP), and Fe concentration in TS7 were higher than the maximum acceptable values in both INWQS Class IIA and DWQSRW. The input of Fe could be resulted from domestic effluent. Na and Mg were well below the acceptable limits of 200,000 and 150,000 μg/L, respectively.

3.3. The variations in physicochemical measurements

Ex-mining ponds can be acidic or alkaline depending on the mineralogy. The measure of acidity or alkalinity of water samples can be numerically expressed with pH, which at lower values become corrosive and have bad taste and harmful impacts on the eyes and skin at high values [58]. In general, the useful nature of any water source is within the pH range of 6.0–8.5 [59]. Based on Table 4, majority of the ex-mining ponds were found to be acidic and may not suitable for domestic uses. Tasik Kelana Jaya (TKJA and TKJB), TB, and TSP were below the DWQSRW and INWQS Class IIA minimum permissible values, and may not be suitable for domestic uses; whereas TPPB had a pH value of 10.0, which was higher than the maximum limit of 9. This could be attributed to the variations in tin ore type and basement rocks, two distinct cassiterites were reported in Puchong area of Klang valley with different dissolutions of the rock formations, which might have contributed to dissimilarity in the levels of pH among other sites [60]. The other man-made lakes showed slightly basic pHs within the tolerable range (Table 5). This is similar to the findings in the Bukit Merah reservoir and Lake Chini with the mean pH values of 7.0 and 6.5, respectively [36,61]. Basically, during the oxidation of metal ores such as FeS_2, H^+ is released, which consequently lowers the pH of the mine water [62]. Meanwhile, carbonates generate pH within the alkaline region [63]. In general, low pH is likely to precipitate metals in solution resulting in high concentrations and impairment of the water quality. Therefore, the acidic water usually contains high concentrations of metals and metalloids like As due to the variations in the environment and mineral ores [64,65]. These rationalize the notable discrepancies found in the As concentrations and pH values between the water samples from the ex-mining ponds and other man-made lakes.

The depletion in DO level is one of the most recurrent effects of pollution in the water bodies [66]. The DO values for the studied lakes were mostly lower than 5 mg/L (INWQS Class IIA), except for TSP and TPPA. The DO values of 3.32, 4.26, and 4.17 mg/L had been previously reported in the ex-mining ponds of Kelana Jaya [33]. This is a threat to aquatic lives as DO is essential for the metabolism of all aquatic organisms. This might be the reason for dead fishes noticed floating in the Kelana Jaya ex-mining pond (TKJA). The low DO in some of the ex-mining ponds could be associated with the low pH value, and the acidic medium was generally found to lower the DO of water samples due to the decomposition of organic matter [36,61,67]. To a certain extent, the waste assimilative capacity of water can be measured with reference to the DO levels [58]. The low DO was likely attributed to the decaying organic matter by bacteria from domestic wastes, as noticed that some of the lakes served as a reservoir for domestic effluents from residences. In this context, BOD is commonly used to assess the contamination of surface water due to domestic and industrial inputs. It is the amount of oxygen needed by bacteria to decompose organic matter under aerobic conditions [68]. In Tables 4 and 5, the BOD values above 6 mg/L (DWQSRW) were observed in TKJA, TKJB, TPPA, Tasik Taman Jaya (TTJA), TSA, and TS7, where Tasik Kelana Jaya and Tasik Shah Alam receive domestic waste from the surrounding residential houses.

The presence of AN in the water bodies is an indication of pollution; it is the level of toxic ammonia presents as a result of leaching or disposal of sewage or manure. The levels of AN showed a range of 0.02–0.48 mg/L and 0.05–0.32 mg/L for the ex-mining ponds and the other lakes, respectively (Tables 4 and 5). The TKJB, TTJA, and TS7 lakes have AN concentrations greater than the INWQS Class IIA maximum limit of 0.3 mg/L. The high AN levels in these sites coincided with the low DO and high BOD values, indicating pollution by organic matter as a result of the flow of domestic effluent and recreational activities. In a similar study, a high AN concentration was reported in the Kelana Jaya ex-mining pond as a result of high loading of organic matter from the sewage [33].

The anthropogenic inputs in surface water determine the quantity of the insoluble particulate matter mostly related to organic particles, surface run-off, sewage, and wastewater [69–71]. The levels of TSS in most of the ex-mining ponds studied in Klang valley are generally low compared with the lakes, and all values were below INWQS Class IIA limit of 50 mg/L. The polluted ex-mining pond TKJB records the highest TSS value of 16 ± 1 mg/L, while TSA was 13.7 ± 0.5 mg/L that could be attributed to the domestic sewage and wastewater from the surrounding residences. In a similar study, the TSS in Chini lake and Bukit Merah reservoir was found to be 8.72 and 1.75 mg/L, respectively [36,61].

The EC indicated the total concentrations of soluble salts in water [72], while the TDS consisted of inorganic salts of chlorides, carbonates, and nitrates of sodium, magnesium, and potassium. The EC and TDS recorded in all studied lakes were below the permissible limits (Tables 4 and 5). In overall, the readings of EC of the most samples from the ex-mining ponds were generally higher than other samples. This could be related to the increasing of the dissolved metals from crushed rocks by the ex-mining activities [54,61,73]. The historically polluted TTJA recorded the highest concentration of TDS and EC among the sites. The TSS concentrations were in the ranges of <5–6.3 mg/L and <5–13.6 mg/L for the ex-mining ponds and other lakes, respectively. These values were below the INWQS Class IIA limit of 25 mg/L.

3.4. Principal component analysis

The variability in the water samples were further explored with PCA. The principal components (PCs), which are usually important with the higher eigenvalues, describe the larger variation in the entire data set [43]. In this study, the PC1 and PC2, respectively, accounted for 26.6% and 18.3% of the total variance. The PC loadings indicate the directions and strength of the variations of those selected water quality parameters whereas the scores summarize the relationships among the samples. The loadings of PC1 contained positively correlated parameters, which comprised As, Cd, Pb, Mg, Ca, TDS, pH, and EC as the major contributors (Fig. 2). This is indicative of the heavy metal pollution, which is likely related to the previous mining activity considering the heavy metals associated with mining and dissolution of the surrounding minerals such as silicates and carbonates. For example, arsenic sulphide minerals are the origin of As in the mine waters [74], other heavy metal ores of Pb and Cd, or in association with primary mineral as impurities are also released to the solution in the same path [75]. Besides that, the dominance of Ca over Na also suggested that weathering was one of the main sources of metals in the water samples [76]. The weathering and dissolution of rocks has been associated with the release of Ca and Mg (Eqs. 3 and 4) into surface waters [77,78], while dominance of silicate minerals (Eq. 5) is the main sources of Na ions in the lakes [79]. Therefore, the hydrochemical process that determines the water quality of the lakes is weathering and dissolution of the carbonate and silicate minerals [80].

$$2FeS_{2(s)} + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1)$$

$$4FeAsS_{(s)} + 13O_2 + 6H_2O \rightarrow 4Fe^{2+} + 4SO_4^{2-} + 4AsSO_4^{3-} + 12H^+ \quad (2)$$

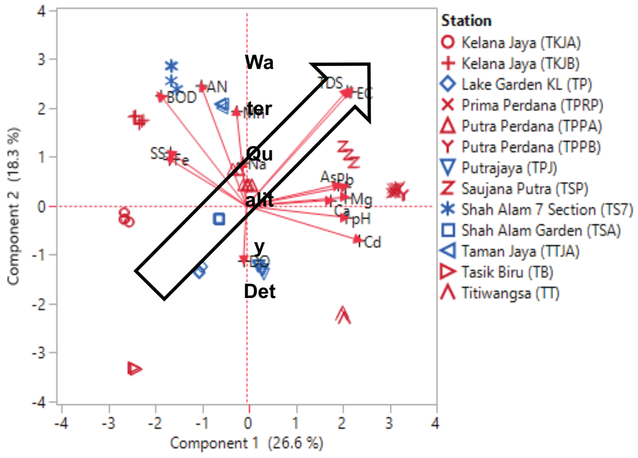

Fig. 2. PCA bi-plot of metals and physicochemical parameters.

$$CaCO_{3(s)} + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (3)$$

$$Mg_2SiO_{4(s)} + 4H^+ \rightarrow 2Mg^{2+} + H_4SiO_4 \quad (4)$$

$$2NaAlSi_3O_{8(s)} + 2H_2CO_3 + 9H_2O \rightarrow 2Na^+ + 2HCO_3^- + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4 \quad (5)$$

By comparing the scores and loadings (Fig. 2), it can be inferred that the ex-mining ponds TPRP, TPPB, and TSP were highly loaded with hazardous metals associated with the mining activity. Again, this rendered the water unfit for neither domestic nor recreational activities. PC2 had high positive loadings for Mn, BOD, TDS, AN, and EC and high negative loadings for DO, which are indicative of pollution as a result of the domestic effluent discharges. Hence, the scores on PC2 showed that TKJB, TTJA, and TS7 were polluted mainly by domestic sewages. Generally, the PCA bi-plot separates the PCs into two parts showing deteriorating of water quality based on metals (PC1) and organic pollutants (PC2). This finding shows the dominance of heavy metals in ex-mining ponds, and suggested their association with leaching and weathering of rocks.

3.5. Hierarchical cluster analysis

The essence of applying HCA was to identify the grouping among the sampling sites and determine the specific contaminated sampling locations based on the pollution levels [81,82]. Fig. 3 gives a dendrogram based on the water quality properties at each sampling site with respect to the variations in the physicochemical and metals' concentrations. Two main clusters showed the influence/dominance of the pollution sources on water quality as suggested in PCA. Cluster 1 was associated with domestic contamination while Cluster 2 was characterized by high metal concentrations (that were related to ex-mining activities). The sub-clusters revealed a similarity in terms of the degree of pollution among the linked sampling sites. Within Cluster 1, TS7 was distinguished as the most polluted sampling sites; followed by TTJA, TKJB, TSA that showed similar patterns of contamination, and another sub-cluster consists of TP, TB, and TKJA.

3.6. Linear discriminant analysis

LDA was used to determine the parameters that distinguish the water samples from the ex-mining ponds and other man-made lakes. The model constructed with the training set gave a precise prediction with $R^2 = 1.000$, with no misclassification shown with the validation set. In Fig. 4, water samples from the ex-mining ponds were perfectly separated from others in the direction of Canonical 1. In this context, Mn, Cd, Ca, and As were highly associated with the ex-mining ponds, while pH, Fe, Mg, Na, and EC were associated with the other lakes. This suggests that the mining activity introduces toxic heavy metals there by significantly affecting the useful nature of the surface water quality [75]. Hence, the need to improve the water quality by metal removal and treatment processes for its proper utilization.

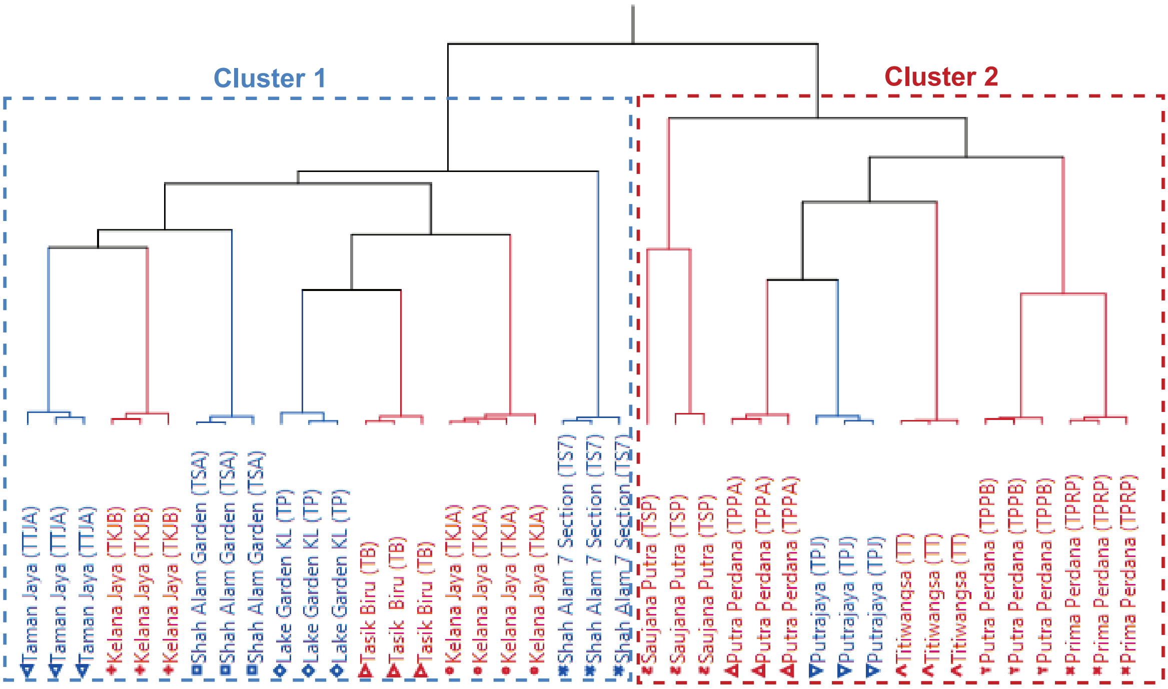

Fig. 3. Schematic dendrogram on the level of pollution in man-made lakes.

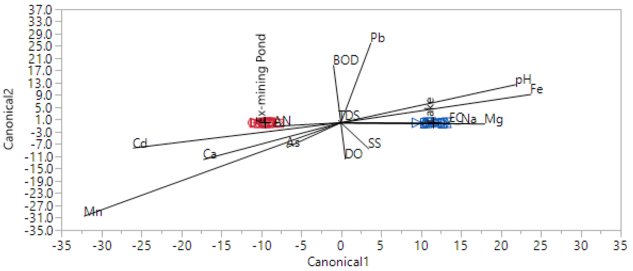

Fig. 4. Canonical plot for the discrimination of water samples between ex-mining ponds and other lakes.

3.7. Remediation and treatment of ex-mining water

Considering the absence of detailed results of studies on the analysis and monitoring of the Malaysian ex-mining ponds, this research presented an important pace in establishing the decision on the utilization of water from the ex-mining ponds for drinking or domestic purposes considering the variations in the level of pollution. Moreover, it will provide an idea for handling mine water with regard to suspected pollutants (heavy metals and physicochemical parameters) after a successful completion of a mine operation.

The treatment of ex-mining water was recommended by researchers [10,83], but the process is expensive. The choice of the appropriate method of treating mining water is a combination of economic and technical considerations; the robustness of the treatment process was normally considered in the final decision. Most of the processes remove the metals by rendering them insoluble using available chemicals such as $Ca(OH)_2$ or by the use of chemicals present in the mine water such as sulphates. However, the best available technique for the treatment of mine water is precipitation achieved by alkali addition, which involves two stages, rendering the metals insoluble and then separating them from the treated water by the use of clarifier. The chemical precipitation methods can be achieved especially when there are high metal loadings [84]. The phytoremediation of the ex-mining water samples was carried out in the Malaysian ex-mining catchment, and considerable concentration of heavy metals was removed [85]. The treatment of ex-mining water to remove the toxic metals was also carried out in some countries, among which is Norway. Between 1985 and 1995, Cu and Fe were extracted from the ex-mining water at “Kings mine”, and this was expensive [86]. The sulphate-reducing bacteria was also used to improve the quality of mine water in a bench-scale experiment, where the pH increased and dissolved concentrations of Fe, Cu, and Zn were drastically reduced [87]. The detailed chemical and biological heavy metal removal processes of acidic mine drainage in wetlands were suggested [88].

Based on the results of the PCA and LDA, As, Cd, Pb, and Mn are the target heavy metals present in the water samples. According to HCA, these metals are of significant levels in Cluster 2 predominantly consisting of the ex-mining ponds (TPPA, TPPB, TT, TPRP, and TSP). The removal of the metals to significant degrees must be taken into considerations as some metals are easily precipitated than others [89].

4. Conclusion

Considerable variations were noted in the metal concentrations and physicochemical characteristics of water samples obtained from the man-made lakes in the Klang Valley. The PCA and HCA suggested that such variations can be attributed to the past mining operations, current domestic inputs as well as the degree of contamination. In the LDA, Cd, Mn, pH, and Fe were identified as the key parameters that discriminate between the water samples from the ex-mining ponds and other man-made lakes; Mn, Cd, Ca, and As were associated with the ex-mining ponds. The concentrations of hazardous As and Cd in the samples from the ex-mining ponds were found mostly higher than the Malaysian DWQSRW and INWQS Class IIA recommended levels. This made the water unfit neither for consumption nor for domestic uses.

The presence and variations of toxic heavy metals in the ex-mining ponds were due to the interaction between the mineral ores with oxygen and other environmental factors, also with the application of chemical substances in the ore separation and concentration, beneficiation and enrichment processes. However, the dilution of ex-mining ponds by a continuous flow of water for flood retention lowers the heavy metal concentrations and raises the level organic pollutants. Of the utmost importance are the managing and treatment of the ex-mining water as recommended by the findings of researchers. The water from the ex-mining ponds of the Klang valley needs to undergo sufficient metal removal processes before any decision is considered on its utilization.

This study also showed the importance of chemometric techniques in analyzing and interpreting the complex water quality data for the decision-making on the effective management and utilization of water resources.

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