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Original Research

Past Metal(loid) Pollution Records Inferred from the Sediments of Bukit Merah Reservoir Perak, Malaysia

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Abstract

Anthropogenic activities, especially due to agricultural practices, tourism, and other land-use forms, have resulted in serious pollution of Bukit Merah reservoir (BMR), the oldest artificial reservoir in Malaysia since the 1980s. This study assessed the past ecological conditions of the reservoir using ^{210}Pb, dating techniques, selected metals, and physicochemical analysis of the sediment core to better manage the reservoir. ^{210}Pb results indicated 34 years of human impact on the reservoir, with arsenic recording the least concentrations in the 1980s and the highest concentrations in 2016 and 2018. The minimum and maximum concentrations of lead and cadmium were found in 1990 and 2009. Whereas Copper and Zinc, concentrations peaked in 2012. The mean EF values of metals in the sediment core were above 1 (EF>1), indicating anthropogenic sources. The I_{geo} values of Arsenic and Cadmium ranged from uncontaminated to strongly contaminated, uncontaminated to moderately contaminated for Lead, Zinc, and Copper. Overall, the dated sediment of BMR revealed that human population growth and increasing economic and agricultural activities coupled with poor land-use forms at the catchment area are the main source of pollution to the reservoir. Therefore, regular monitoring and the enforcement of relevant environmental laws are needed to manage the reservoir.

Keywords: heavy metals, lake sediment, anthropogenic activities, environmental change, ^{210}Pb dating

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Introduction

In the last few decades, the catchment area of Bukit Merah Reservoir (BMR), the largest artificial reservoir in Peninsular Malaysia, has been subjected to increasing human activities, including agricultural activities, tourism, sand dredging, and the construction of small and medium-scale industries, among others [1]. Consequently, pollutants resulting from these activities in the catchment area are transported into the reservoir, making the bottom sediment a potential archive and source of different substances, including organics and trace metals [2].

Heavy metals are of major concern as contaminants of aquatic ecosystems due to their toxicity, environmental persistence, and the potential to bioaccumulate in foods [3-5]. Sediments contaminated by toxic metals are major threats and can directly affect the sediment-dwelling biotas, wildlife, and human health due to their harmful nature [6-10]. What's more is that under changing lake environmental conditions, for example, changing redox conditions caused by seasonal eutrophication, sedimentary toxic metals can be released into the above water column, increasing bioavailability [11-14].

Some important studies on the heavy metal pollution in freshwater ecosystems of Malaysia are those of [15], who identified cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), manganese (Mn), and chromium (Cr) as the major causes of water contamination in Lake Chini. [16] reported high levels of Cd and Zn in the range of 3.0-37.9 $\mu g\ g^{-1}$ and 71-374 $\mu g\ g^{-1}$ in the Langat River, Negeri Sembilan. Results of a heavy metal study in the Juru River [17], compared to average global shale values [18], showed that Cu, Pb, and Zn concentrations were higher than natural shale values of 45 $\mu g\ g^{-1}$, 20 $\mu g\ g^{-1}$, and 95 $\mu g\ g^{-1}$, indicating that the river is heavily polluted with heavy metals.

In many lakes where long-term monitoring data is lacking or unavailable, studies of variation in contaminant concentrations in a dated sediment core can be used to trace the past ecological status of the lake [19], because lakes serve as sinks for different types of anthropogenic pollutants carried from various environmental sources [20-23], and in such depositional events, sediments become a source of chemical records which is utilised in the reconstruction or tracing of local pollution history [24-28]. Such information from reconstruction studies is vital to improving lake management plans and policy formation [29]. Therefore, it becomes important to establish a stable chronology of lake sedimentation for the previous years to give useful information on the past conditions of the aquatic ecosystem and set restoration targets since a lack of data on the degree to which sediment is polluted poses a health risk to both the human and aquatic environment [30, 31]. As such, the application of short-lived radioisotopes of ^{210}Pb is mainly useful in establishing the age of sediment layers and investigating the extent of human impacts on the aquatic ecosystem [14, 32].

Most studies on the Bukit Merah reservoir have mainly focused on the physicochemical parameters of the reservoir [33-35]. No research establishing the past metal pollution trend from the sediment core of the reservoir has been conducted. Hence, the objective of this study is (1) to establish the stratigraphic trend of metal concentration in the sediment core of Bukit Merah reservoir and (2) to establish sediment chronology using ^{210}Pb dating techniques through the conversion of sediment depth profile and chemostratigraphy into timescales that could be correlated to documented events based on sediment characteristics, (3) to establish metal enrichment factors, to determine if the sources of metals, whether anthropogenic or not, (4) to establish the relationship, if any, between chemostratigraphy, grain size, and organic matter. This research is the first attempt to integrate ^{210}Pb dating techniques to understand past events in the BMR watershed to establish a baseline to manage the ecosystem.

Materials and Methods

Study Area

The Bukit Merah reservoir (050 01 “35.42”N, 1000 39 “42.92”E), located 65 km south of Penang and 95 km north of Ipoh, was constructed in 1902 with a capacity of 70 million m^3. The reservoir has a mean depth of 2.5 m, and accounts for an area of 33 km^2 out of a total catchment area of 408 km^2 [36]. The reservoir is part of the Kerian Irrigation Scheme for the cultivation of about 24,000 ha of paddy fields and serves as a domestic water supply to the inhabitants of the Kerian and Larut Matang districts [2]. The lake also acts as a flood pause and drought control, as well as a tourist attraction since the construction of Lake Town Resort in the 1990s. The outlet from BMR also releases water to the sites used for Arowa fish farming [36].

Sample Collection

Following a bathymetric survey in November 2019, two 25 cm cores (Fig. 1) were recovered from the lake at a water depth of 2.6 m using a gravity corer with an internal diameter of 9 cm. The cores were held in a vertical position to avoid mixing and transported to the laboratory, sub-sampled at 1 cm intervals, and kept in whirl-pak® at approximately 4ºC. Following this, all sediment samples were freeze-dried at -50ºC using Labconco 6-litre benchtop freeze-dryer system, grounded and homogenised by mortar and pestle, then filtered through a sieve of 100 µm mesh size preceding analysis.

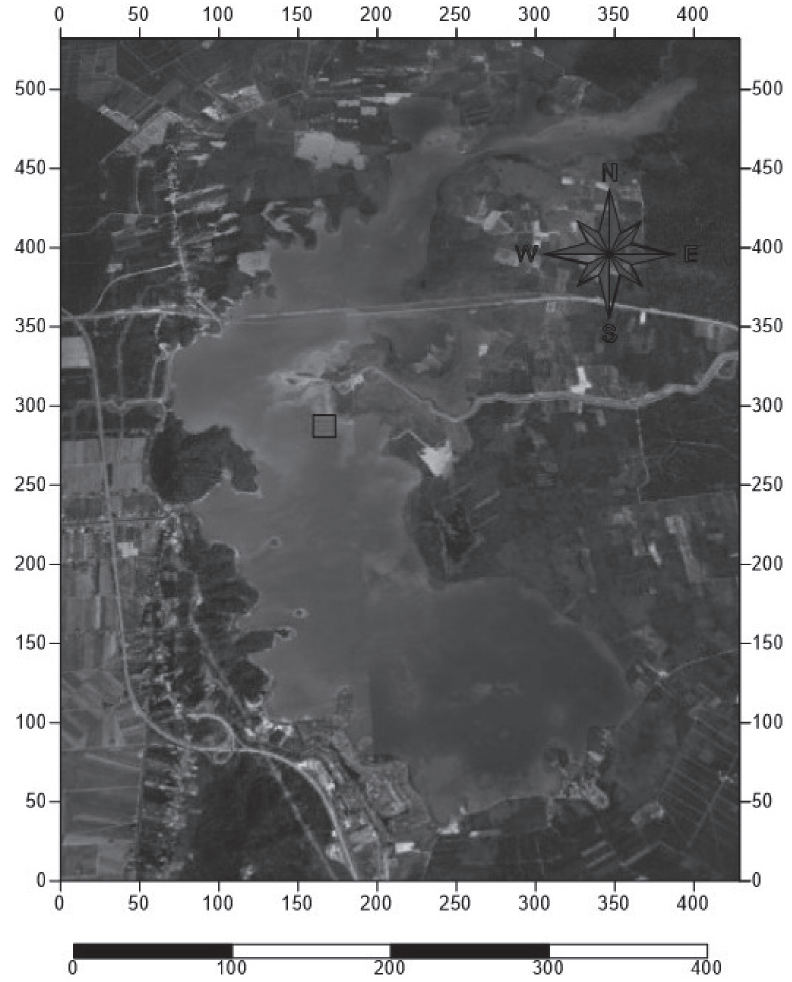

Fig. 1. The study area showing Bukit Merah reservoir in blue colour and Sampling site indicated by a square.

Dating of Sediment Core

Freeze-dried samples of sediment core BMR1 were examined for ^{210}Pb, ^{137}Cs, ^{226}Ra, and ^{241}Am using a direct gamma assay, by an ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector in the Environmental Radiometric Facility at University College London. ^{210}Pb was established by its gamma radiation at 46.5keV and ^{226}Ra by the 295keV and 352keV gamma beams of light produced by its daughter nuclide of ^{210}Pb after being stored in closed containers for three weeks to permit radioactive equilibration. ^{241}Am and ^{137}Cs were determined by their radiations at 59.5keV and 662keV [37]. The total accuracy of the detector was established by standardized sources of sediment samples of well-known activity. Adjustments were made for the impact of self-incorporation of low-energy gamma emissions within the sample [38]. Unsupported ^{210}Pb was computed by deducting ^{226}Ra activity (as unsupported ^{210}Pb) from the total ^{210}Pb activity. Sedimentation rate and ^{210}Pb chronologies of the core were computed employing the CRS (constant rate of ^{210}Pb supply) dating model [39], by linear regression between excess ^{210}Pb and core depth.

Metal Analysis

Trace metals (As, Pb, Cd, Cu, Fe, and Zn) were analysed by weighing about 0.5 g of freeze-dried sediment samples into Teflon. Aqua regia solution of HNO_3 (65%): HCl (35%) (7:3) was prepared and poured into the Teflon. The samples were digested in a microwave digester at a temperature range of 200ºC to 300ºC for about 4 h. Digested samples were left to cool, then passed through a 0.45μm Whatman grade 1 filter paper and made up to a 50 cm^3 volume with distilled water. The digested sediment samples were analysed for metals using an ICP-OES (Agilent Technologies 700 series). The accuracy of metals analysed was accessed with standard sediment reference materials (SUD-1, Environment Canada, National Water Research Institute, Canada) with recoveries between 92% and 108%. For analytical precision, 3 replicates of a homogenised sample of each metal were analysed per run. Moreover, standards and blanks were frequently run with each sequence of analyses to corroborate the data obtained by methods described.

Determination of Physico-Chemical Parameters

Sediment grain size fraction was estimated by [40]. In brief, approximately 10 g of dried sediment samples were measured into a conical cylinder, stirred together with distilled water, and filtered through a sieve of 63 µm mesh size. The sediment held by the sieve was oven-dried at a temperature of 105ºC for 24 hours and dry weight (DW) was determined as the proportion of sediment with a grain size fraction larger than 63 µm based on equation 1.

$$< 63\mu m\ (\%) = \frac{W_i - W_r}{W_i} \times 100 \tag{1}$$

Where w_i represents the original 10 g weight of sediment and w_r is the weight of the sediment held by the sieve.

Organic matter was determined by the loss on ignition (LOI) method [41]. Briefly, about 10 grams of dry sediment samples were measured into porcelain crucibles, then burned in a furnace at a temperature of 550ºC for 4 h. The organic matter content was combusted to ash and carbon dioxide was released. Triplicate samples were used to estimate the organic content of the sediments and their mean and standard deviation values were recorded. The combusted samples were cooled in a desiccator to eliminate moisture content before being weighed again. Organic matter composition was calculated based on equation 2 [41].

$$\mathrm{LOI}_{550} = \frac{DW_T - DW_{550} \times 100}{DW_T} \tag{2}$$

Where LOI_{550} represents the percentage LOI at 550ºC, DW_T Original dry weight of the sample before burning and DW_{550} is the dry weight sample after combustion at 550ºC in the furnace.

About three-quarters of a full sediment sample was measured into a beaker containing about 30 ml distilled water. The sample was stirred vigorously, and the mixture was left to settle for about 10 minutes to allow the sediment sample to dissolve. A pH-meter was standardized with a buffer solution of pH 7 and was inserted into the wet sediment mixture and pH was recorded [42].

Determination of metal enrichment in the sediments geochemical index (Igeo) and enrichment factor (EF) were applied to study the change in the pollution level of metals with respect to sedimentary processes and depth of sediment core. Trace metal concentrations at the base of the BMR 2 sediment core correspond in time to about three decades before the present; therefore, they are not suitable as pre-industrial backgrounds. As such, Continental Shale values [43] were utilised as background values for the computation of Igeo and EF. The background values used include (Cu = 45, Cd = 0.3, Pb = 20, Fe = 47,200, Zn = 95, and Ni = 68). Thus, Igeo was computed from equation (3) below

$$I_{geo} = Log_2\, C_n/1.5B_n \tag{3}$$

Where C_n represents the determined concentration in the sediment for metal n. B_n is the baseline value for the metal n. [44], while factor 1.5 was applied to stabilize possible variation in baseline values due to the lithological process. The geochemical index was categorised in to six classes according to [45] namely, $l_{geo} \leq 0$ = unpolluted, $0 < l_{geo} \leq 1$ = unpolluted to moderately polluted, $1 < l_{geo} \leq 2$ = moderately polluted, $2 < l_{geo} \leq 3$ = moderately to highly polluted, $4 < l_{geo} \leq$ highly to very highly polluted, $l_{geo} > 5$ = very highly polluted. The EF value was computed from equation (4):

$$\mathrm{EF} = \frac{M}{Fe}(sample)\ \mathrm{X}\ \frac{Fe}{M}(baseline) \tag{4}$$

Where '(M/Fe) sample' is the ration of the measured metal to Fe in the study sample, while '(Fe/M) baseline' is the natural baseline value of the total metal to Fe ratio [46]. EF assessments were grouped in to five enrichment standard values [46], namely, EF <2: deficiency to minimal enrichment; EF = 2 – 5: moderate enrichment; EF = 5 – 20: significant enrichment; EF = 20 – 40: very high enrichment; EF > 40: extremely high enrichment.

Statistical Analysis

Pearson correlation analysis was used to study the association between trace metals and physicochemical properties of the sediment, their sources, and pathways.

Results

Sediment ^{210}Pb Chronologies

The total ^{210}Pb activity from Bukit Merah reservoir indicated a reduction in Unsupported ^{210}Pb activities which was non-monotonic and did not reach the base of the core (Figs 2(a, b)). Sediment accumulation rates through the core fluctuated around a mean of 0.23 g cm^{-2} yr^{1}, with the highest rate of 0.37 g cm^{-2} yr^{1} occurring in the 1990s. The CRS model assigned a 34-year age to the oldest sediments at 22.5-24.5 cm (Fig. 3, Table 1). ^{241}Am activities were found at two disconnected samples, while an independent marker of ^{137}Cs used to corroborate the height of atmospheric nuclear fallout of 1963 was not detected in BMR sediment core (Table 2).

Mean Trace Metal Concentrations and Stratigraphic Trend in the BMR Sediment Core

The mean concentration of metals in the sediment core of BMR is presented in Table 3. The results showed that the average content of arsenic (As) ranged from 8.45 to 12.58 mg/kg with a mean of 10.42 mg/kg; cadmium (Cd) levels ranged from 0.39 to 1.03 mg/kg with an

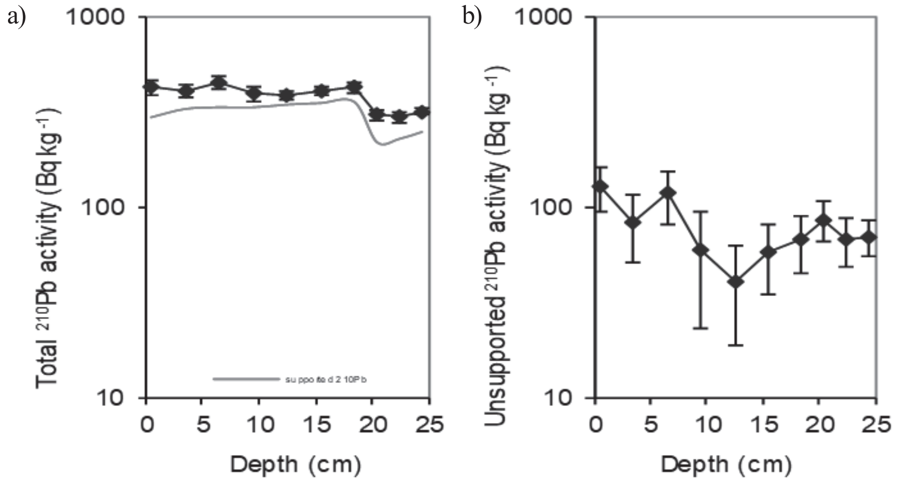

Fig. 2. Fallout radionuclide concentrations in sediment core BMR1 from Bukit Merah Reservoir, Malaysia, indicating a) background ^{210}Pb and b) unsupported ^{210}Pb concentrations against depth.

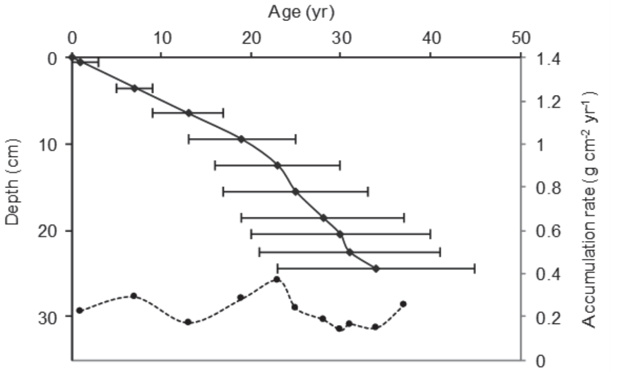

Fig. 3. Sediment age chronology of sediment core BMR1 core from Bukit Merah Reservoir Malaysia, showing sediment accumulation rate and the CRS model ^{210}Pb dates. The dash line indicates sedimentation rates, while the solid line shows chronologies.

average of 0.68 mg/kg; copper (Cu) levels ranged from 0.92-2.62 mg/kg with a mean of 1.61 mg/kg; lead (Pb) concentrations were in the range of 8.90-16.35 mg/kg with an average of 12.76 mg/kg; zinc (Zn) contents ranged from 20.45-35.80 mg/kg with an average of 27.94 mg/kg; and iron (Fe) concentrations varied from 31.50-58.94 mg/kg with an average of 44.95 mg/kg (Table 2). Fig. 4 depicts the stratigraphic concentration of metals, which showed that total As decreased from 8.45 mg/kg in 1986 (24 cm) to 8.91 mg/kg in 1988 and then increased to 10.38 mg/kg in 1995 (14-18 cm). As concentrations thereafter increased overall and reached a peak value of 12.59 mg/kg in 2018 (1-3 cm). Cd recorded the lowest concentrations of 0.39 mg/kg at a depth of 22-24 cm, which corresponds to the year 1987, followed by a steady increase to 0.49 mg/kg in

Table 1. ^{210}Pb chronology of sediment core BMR1 from Bukit Merah Reservoir, Malaysia.

Depth	Dry mass	Chronology			Sedimentation		
cm	gcm^{-2}	Date (AD)	Age (Yr)	±	gcm-^{2}yr^{1}	Cm yr^{1}	± %
0	0	2019	0				
0.5	0.2571	2018	1	2	0.229	0.468	33.6
3.5	1.7136	2012	7	2	0.2931	0.638	45.4
6.5	3.0141	2006	13	4	0.1745	0.392	41.6
9.5	4.3843	2000	19	6	0.2848	0.662	68.5
12.5	5.5958	1996	23	7	0.37	1.14	64.7
15.5	6.3313	1994	25	8	0.2393	1.102	55.1
18.5	6.8984	1991	28	9	0.1895	1.091	53.7
20.5	7.2001	1989	30	10	0.1409	0.985	50.2
22.5	7.4703	1988	31	10	0.1684	1.078	54.3
24.5	7.8247	1985	34	11	0.1519	0.882	53.7

Table 2. Artificial fallout radionuclide concentrations in core BMR1.

Depth	Cs-137		Am-241	
cm	Bq Kg^{-1}	±	Bq Kg^{-1}	±
0.5	0	0	0	0
3.5	0	0	0	0
6.5	0	0	0	0
9.5	0	0	0	0
12.5	0	0	0	0
15.5	0	0	4.95	1.86
18.5	0	0	0	0
20.5	0	0	0	0
22.5	0	0	0	0
24.5	0	0	2.97	1.14

1989 (18-21 cm). A rise in Cd concentration occurred from 0.58 mg/kg in 1990 and peaked in 2009 (3-5 cm). The lowest concentration of Cu 0.98 mg/kg was observed at a depth of 23 cm, corresponding to 1986. Afterward, Cu increased steadily between 1991 and 2001 with an average value of 1.78 mg/kg, followed by a steady increase to the peak value of 2.62 mg/kg in 2010 (2-3 cm). Pb concentrations in the core ranged from 11.50 mg/kg (18-20 cm) in 1989 to 16.75 mg/kg (1.5-2.5 cm) in 2014. Unlike other metals, Pb concentrations were high all through the core, increasing from the bottom to the top of the core. Zn concentration gradually increased from a low of 20.45 mg/kg in 1988 (20-22 cm) to a high of 35.68 mg/kg in 2017 (0-2 cm). Exceptions can be seen between 1995 (13-15 cm) and 2005 (6-8), where Zn levels shifted from 30.58 to 33.58 mg/kg. Fe concentration reached a minimum level of 35.40 mg/kg (23-24 cm) in 1986, followed by a constant increase between the years 1988 (20-21 cm)

Table 3. Mean and range of heavy metal concentrations in the sediment core of Bukit Merah Reservoir, compared with selected reservoirs worldwide.

	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Reference
Bukit Merah reservoir, Perak Malaysia	(8.45-12.59) 10.42	(0.39-1.03) 0.68	(0.92-2.62) 1.61	(8.90-16.35) 12.76	(20.45-35.80) 27.94	(31.50-58.94) 44.95	This study
Carlos Botelho- Broa reservoir, Brazil	25.40	-	32.65	12.80	40.39	52,411.36	[55]
Three Gorges reservoir, China	79.7	0.3	27.2	30.2	-	-	[56]
Gunsan reservoir, South Korea	72.2	0.26	29.2	30.1	96.6	-	[57]

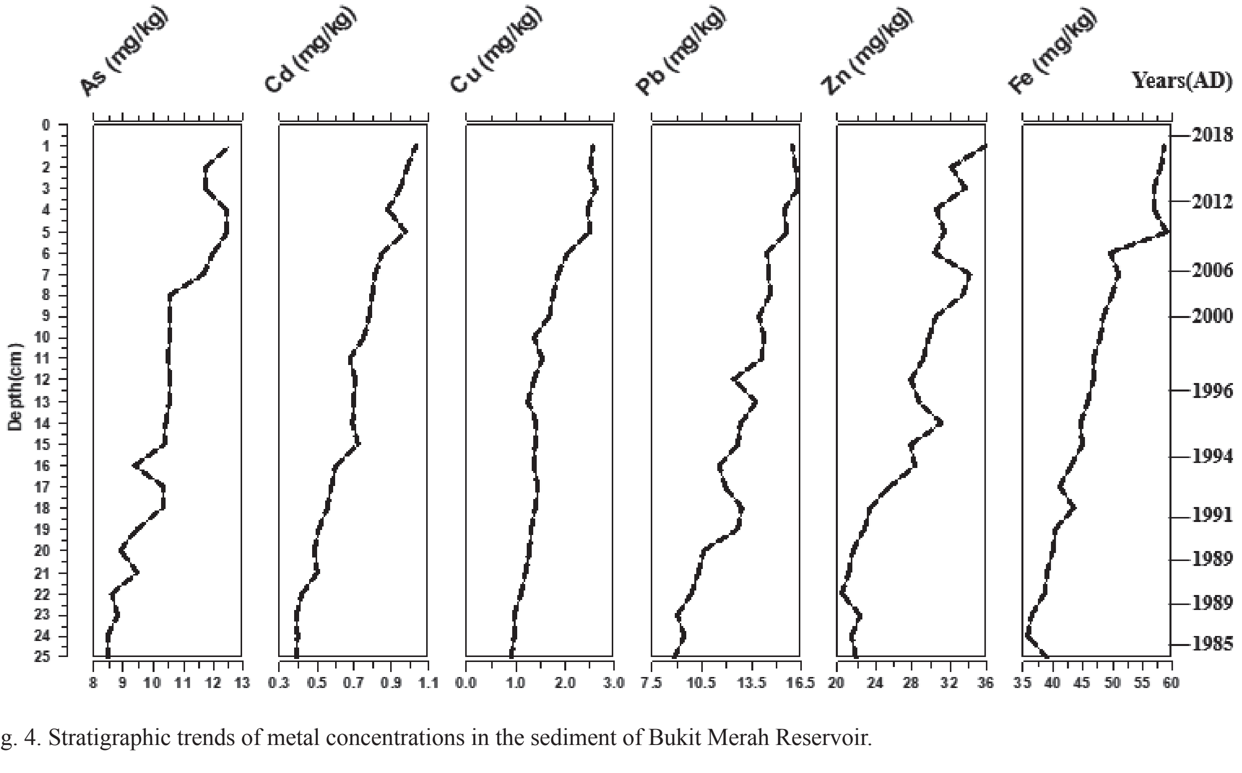

Fig. 4. Stratigraphic trends of metal concentrations in the sediment of Bukit Merah Reservoir.

and 2005 (6-7 cm). Fe concentrations peaked in 2009 (4-5 cm), followed by a gradual rise to the top of the core.

Physical and Chemical Parameters of BMR

The physical and chemical parameters of the sediment core retrieved from BMR are presented in Table 4. Results showed that a maximum pH value of 6.8 was recorded at a depth of 1-3 cm, while a minimum value of 5.7 was detected at a depth of 1 3-15 cm. The pH value of the entire core length indicated an acidic condition. The lowest percentage of organic matter was obtained at a depth of 7-8 cm with a value of 1.6%, while the highest percentage of organic matter was detected at a depth of 16-18 cm and 23-25 cm with a value of 2.9%. Generally, the results of the organic matter assessment revealed that the level of organic matter available in the sediment samples was relatively high. Similarly, the finest grain size fraction (63%) in the BMR sediment core ranged between 45.2% (3-6 cm) and 53.6% (7-10 cm).

Table 4. Mean pH, organic matter composition and sediment grain size in Bukit Merah Reservoir core.

Depth (cm)	pH	Organic matter (%)	Fine grain size (<63 µm %)
0.5	6.5	0.90	46.8
3.5	6.8	1.1	45.2
6.5	6.6	1.3	50.5
9.5	6.4	1.6	53.6
12.5	5.9	1.9	47.8
15.5	5.7	1.7	43.8
18.5	6.1	2.9	44.8
20.5	5.6	2.5	45.8
22.5	5.9	2.6	46.2
24.5	6.2	2.9	47.6

Sediment Enrichment Factors

The I_{geo} values for As were uncontaminated between ca. 1986 and 1987 and then raised to moderate contamination in 2010 (Fig. 5). Following 2010, As became highly contaminated (I_{geo} 3.2) until 2012, when it returned to a moderate level of contamination until around 2018. The Igeo values for Cd indicated moderate contamination (1-2) throughout the BMR2 core except in ca. 1986 and 1987 where the I_{geo} values were uncontaminated (0-1). I_{geo} for Cu varied between uncontaminated and moderate contamination. I_{geo} for Cd was uncontaminated between ca. 1985 and 1988, then increased steadily from ca. 1990 to the top of the core where Igeo was moderately contaminated (1≤CF<3). Igeo for Pb was moderately contaminated in ca. 1985 and 1986 but became strongly contaminated from ca. 1990 to ca. 2017. Igeo for Zn was uncontaminated in (ca. 1986, 1988, 1995, 2004, 2012, and 2015) and became moderately contaminated in the rest of the core section (Fig. 5). Similarly, the EF values for Cd, As, Cu, Pb, and Zn (Fig. 5) varied between 1.02 to 1.35, 0.97 to 1.28, 0.98 to 1.09, 0.92 to 1.10, and 0.98 to 1.06, respectively. Generally, the EF value was greater than 1 (EF>1) throughout the core, indicating that metal enrichment in BMR may have been influenced by the industrial and agricultural activities taking place in the catchment area.

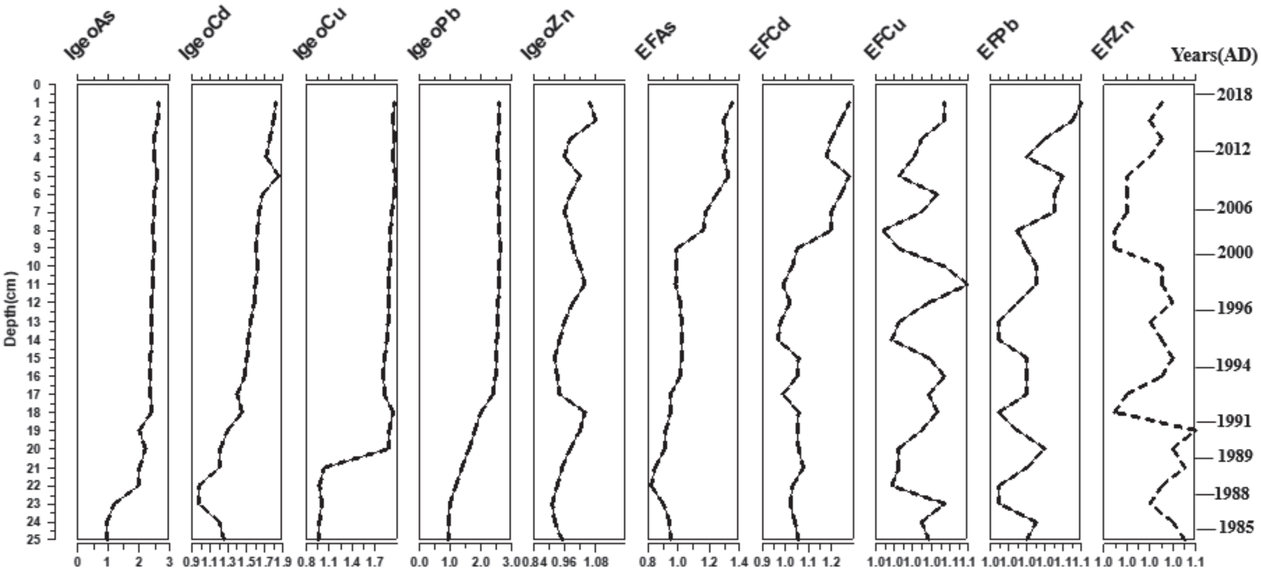

Fig. 5. Variation of geo-chemical (I_{geo}) and enrichment factors (EF) of Bukit Merah Reservoir.

Discussion

Sediment Chronology

Substantial excess ^{210}Pb activity at the base of the recovered core showed a high sedimentation rate (Table 1). Indeed, the average sedimentation rate determined in BMR was higher compared to other reservoirs in Southeast Asia [47,48]. The reservoir, which has been undergoing serious sedimentation problems since 1984, was still highly degraded until 2018, showing severe erosion and siltation [49]. The subsurface peak of excess ^{210}Pb at 12.5 cm might have been produced by sediment mixing and re-suspension associated with the ageing of the reservoir [50]. Also, bioturbation, which results from the burrowing of organisms, may cause the mixing of newly accumulated sediment with older sediment deposits [51]. The transportation of sediments and substantial change of sediment texture due to burrowing animals is the most common type of bioturbation described in most aquatic environments [52]. In this study, however, no substantial change in sediment texture was observed along the sediment layers. Nevertheless, we acknowledge that the sediment ages of the BMR core were derived by the CRS (constant rate of ^{210}Pb supply) dating model [53], which places the age of the reservoir at 34 years of human impacts. The absence of ^{137}Cs and the presence of a small amount of ^{214}Am in the sediment core also collaborate with our dating results that the sediment deposition is young and couldn't have recorded the nuclear fallout peaks of 1963 (39). To our understanding, no research on sediment chronology has been carried out in the Bukit Merah reservoir, thus comparison is not possible.

Heavy Metal Distribution and Enrichment

Heavy contamination originates from a wide range of anthropogenic and natural sources, including atmospheric deposition, geological weathering, municipal and industrial discharges, power generation, and agricultural run-offs [54]. In this study, the average concentration of heavy metals in the BMR1 core was lower compared to other impacted reservoirs worldwide (Table 2). The difference in the concentration of metals in these reservoirs may be due to the level of industrialization, urbanization, agricultural activities, and other anthropogenic activities taking place in their catchment areas, thereby releasing pollutants into the reservoirs. While BMR is in the rural area of Penang state and is mostly impacted by effluent from chemical fertilisers and other agrochemicals used for the cultivation of palm oil trees, rice, and rubber [2], the Carlos Botelho reservoir, the Three Gorges reservoir, and the Gunsan reservoir are in urban cities, surrounded by heavy industries, commercial and residential facilities, thus, heavy metals in these reservoirs were significantly influenced by urban-related activities [55-57].

The observed stratigraphic trend of heavy metals showed that the levels of heavy metals in the sediments of BMR increase through time with variations. Most of the heavy metals had their lowest values in the sediment deposited during the 1980s. As levels show an increasing trend through time while Cd, Cu, Pb, Zn, and Fe fluctuated (Fig. 4). Presently, industrial activities within the catchment area are not significant. However, intensifying agricultural practices have led to the expansion of palm oil, rubber plantations, and rice paddies [49]. Thus, fertilisers and pesticides, which are commonly used in agricultural activities, are transported through surface runoff into the reservoir [58]. A large proportion of these agrochemicals used in farming processes contain As, Cu, Cd, Pb, and Zn [59]. Some pesticides and fungicides, for example, Mancozeb ($C_4H_6N_2S_4$)2Mn) xZn_y), known for their high metal composition, are often utilised in farming operations in the catchment area [60]. In addition, oil spills attributed to the increasing number of machines engaged in farming operations may be sources of metals, especially Pb, accumulated in the sediment [61]. Available studies also show that increasing tourist activities have led to relatively high metal discharge by motorboats that navigate in the reservoir [34]. Moreover, luxurious private residential houses and a four-star resort located in the lake area tend to discharge grey water containing metals [34]. Population growth and increasing land use activities, including logging, in the upstream area of the lake, are triggering accelerated erosion, high sedimentation, and trace metal-related nutrient loading into the lake [50].

The sources of heavy metal pollution which were evaluated using the geo accumulation index and Enrichment factor showed that the EF values for all the heavy metals in the sediment core of BMR were greater than 1 (EF>1), signifying that the metals were likely to be from anthropogenic sources, which include but are not limited to agricultural activities [62]. The erosion of metal-bearing rocks from nearby hills where mining activities is taking place in the catchment area could steadily increase metal enrichment [63]. On the other hand, the I_{geo} values ranged from uncontaminated to strongly contaminated for As and Cd, and from uncontaminated to moderate contamination for Pb, Zn, and Cu, which may indicate input of metals from related agricultural activities [62].

The contraction in I_{geo} and EF enrichment indices in this study may be due to the use of a shale average instead of local average background values as indicated by some studies [64,65]. However, due to high sedimentation rates in the study area, sediment dating back to times before anthropogenic pressure that substantially altered the catchment area was beyond the reach of the cores, which necessitated the use of average shale values. The use of average crust concentration values may lead to underestimations or overestimations of EF. EF values may vary as the concentration of metals changes. whereas the Igeo

Table 5. Pearson's correlation analysis between heavy metal concentrations, physical and chemical factors in Bukit Merah Reservoir core.

	As	Cd	Cu	Pb	Zn	Fe	OM	<63 µm	pH
As	1.00								
Cd	0.34	1.00							
Cu	-0.37	0.31	1.00						
Pb	0.25	-0.05	-0.19	1.00					
Zn	-0.35	0.09	0.89*	-0.08	1.00				
Fe	0.29	0.36	0.65*	0.32	0.65*	1.00			
OM	-0.03	0.34	-0.05	-0.42	-0.15	-0.15	1.00		
<63 µm	-0.08	0.04	0.13	0.04	0.23	-0.14	-0.17	1.00	
pH	0.24	0.42	-0.09	0.02	-0.19	0.07	0.29	-0.41	1.00

*Correlation is significant at the 0.05 level (2-tailed)

classification of pollutants does not always vary as the content of the metal fluctuates. However, both indices are combined in most studies to give a reliable account of metal sources [66]. Therefore, the Igeo and EF indices were successfully used to access three-decade trends of metal pollution and sediment quality in Bukit Merah reservoir.

Relationship between Heavy Metals, Organic Matter, and Grain Size of BMR

Correlation analysis among pairs of metals indicated a significant positive association ($p<0.05$) between Cu and Zn ($r = 0.89$, $p = 0.001$), which might entail a common source of these metals. A similar relationship was seen between Fe and Cu and Zn and Fe (Table 5). In contrast, results revealed that relationship between Cu and Cd ($r = 0.31$, $p = 0.42$); As and Cd ($r = 0.34$, $p = 0.49$); As and Pb ($r = 0.25$, $p = 0.31$); Cd and Zn ($r = 0.09$, $p = 0.64$), were not significant indicating that these metals may have entered the reservoir from other sources. Additionally, non-significant negative associations were observed for As and Zn ($r = -0.35$, $p = 0.41$); Cd and Pb ($r = -0.05$, $p = 0.72$); Cu and Pb ($r = -0.19$, $p = 0.61$), suggesting different sources for these metals [67]. The potential sources of these metals in the reservoir comprise agricultural activities, metal-bearing rocks, and wastewater, amongst others.

Sediment grain size distribution affects the concentrations of contaminants per unit of sediment mass owing to the greater surface area to mass ratio of fine-grained sediments [68]. Changes in particle grain size distribution with depth in the sediment cores may influence the contamination level in the sediment core [69]. However, in our study, the fine grain fraction (63 microns) was not significant ($p<0.05$) in determining the concentration of heavy metals in the sediment core of BMR. Although this observed pattern of the sediment grain size relationship with metal is unclear, despite the belief that smaller grain size sediment particles are always associated with heavy metals [67], nevertheless, our finding is supported by a similar study conducted in the Miyun reservoir, China by [70], who reported that grain size fraction in the range of 70 to 95% did not influence the level of heavy metal concentration in the sediment of the lake. There was no correlation found between organic matter and heavy metals, indicating that they were not bound to organic matter and accumulated separately [71].

Conclusions

The age-depth profile of Bukit Merah reservoir was reflected by 34 years of human impact on the reservoir dating back to 1984. In the sediment core, concentrations of As varied significantly compared to other studied metals, with the lowest concentrations in the 1980s and the highest concentrations between 2016 and 2018. The concentrations of Cd, Cu, Pb, Zn, and Fe fluctuated with core depth and time. However, all the metals had their lowest concentrations in the 1980s. Heavy metal concentration in the sediment core did not affect the distribution of sediment grain size (<63 µm %). The EF values for all the metals were above 1 (EF>1), indicating that the sources of these heavy metals in the sediment of BMR were most likely from anthropogenic activities. The I_{geo} index for As, and Cd ranged from uncontaminated to strongly contaminated and from uncontaminated to moderately contaminated for Pb, Zn, and Cu. Our finding suggests that the reservoir is undergoing serious deterioration due to an increase in human population, agricultural activities, and poor land use in the catchment area. Therefore, regular monitoring, public awareness campaign, and imposing necessary environmental regulatory laws are needed.

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Conflict of Interest

No conflict of interest was declared by the authors.

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