



Heavy metals in water, sediment, fish and associated risks from an endorheic lake located in Southern Africa

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Abstract

The study assessed heavy metals (Cd, Cu, Fe, Mn, Pb and Zn) and physico-chemical parameters in water, sediments and fish from an endorheic lake (Lake Chilwa) in Malawi. It was observed that pH (max. 9.7), EC (max. 2936 $\mu\text{S}/\text{cm}$), TDS (max. 2119 mg/L), NO_3^- (max. 6.6 mg/L) and PO_4^{3-} (max. 1.3 mg/L) were higher in the dry season than in the rainy season. Pb was not detected in all samples. However, the rest of heavy metals were detected with significant values of Mn and Cu in fish (Mn: 0.015–1.18 mg/kg dry weight, dw; Cu: 0.41–0.92 mg/kg dw) and sediment (Mn: 2.25–10.66 mg/kg dw; Cu: n.d–1.63 mg/kg dw). The concentrations of heavy metals in fish samples were below the maximum limits for edible fish recommended by Food and Agriculture Organization/World Health Organization: Cd (0.1 mg/kg), Cu (3 mg/kg), Fe (43 mg/kg), Pb (0.2 mg/kg), Mn (2–9 mg/kg) and Zn (60 mg/kg). The calculated target hazard quotients (ranged from 0.001 to 1.07) indicated no human risks from fish consumption. Furthermore, dry season values for Mn, Cu and Zn in sediments were significantly higher ($p < 0.05$) than those of the rainy season. Conversely, Fe in sediments was significantly higher ($p < 0.05$) in the rainy season than in the dry season. The use of fertilizer and indiscriminate disposal of metal products contributes to the observed levels. This calls for reinforcement of suitable agricultural and waste management practices in the study area.

Keywords Environment · Heavy metals · Lake Chilwa · Pollution · Wetland

Introduction

The pollution of freshwater has become a global problem in recent years. It is a known fact that in most water bodies tons of wastewater from various sources is deposited every day (United Nations World Water Assessment Programme, UN WWAP 2003). This pollution of water bodies is extreme in least developed countries due to mainly the absence of wastewater treatment systems. The pollution of water bodies in least developed countries introduces wastewater (at times up to 70% untreated industrial effluent) in water bodies contaminating lotic waters (UN-Water 2009). Coastal areas are very prone to being contaminated by industrial activities as they receive water from rivers that have been polluted by virtue of passing through industrial areas (Khan et al. 2017). Contaminants like heavy metals that are mainly from human activities end up polluting coastal areas (Rate et al. 2000). According to Gupta et al. (2009), the contamination of water bodies by such contaminants as heavy metals tend to be exaggerated in areas where there is heavy industrial activity and agriculture in addition to population pressure and lack of

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proper enforcement of environmental rules and regulations. The problem with heavy metals is that they are among the most toxic chemicals (Wepener et al. 2001). Since the heavy metals are toxic, once they contaminate water, sediment and fish, they render these not safe to the health of organisms (Ahmad et al. 2010). Heavy metals are not volatile; as such, they tend to bind to sediments or particles. As such, a lot of organisms including algae and bacteria, which feed on fish, end up picking heavy metals (WHO 2011). Heavy metals tend to bioconcentrate; as such, fish may have higher levels than their vicinity (Olaifa et al. 2004). A number of studies have confirmed the bioconcentration of heavy metals in fish in several countries including Turkey (Demirak et al. 2006).

Malawi as a country has adopted the United Nations Sustainable Development goals by incorporating them in various government policies. One of which is to increase exports for the country in a sustainable manner. This has led to deliberate policies, which aim at increasing industrial development. As such, the country is fighting hard to increase both foreign and indigenous investments in those areas that are more productive (Government of Malawi 2006). This will lead to an increase in both industrial and agricultural productivities with a high chance of heavy metal pollution to water bodies.

Contamination of African lakes by heavy metals mainly from human activities has been reported by a number of authors. These include Lake Léré of Chad (Mahamat et al. 2017); Asejire of Nigeria (Jenyo-Oni and Oladele 2016); Manzala, Edku and Borollus of Egypt (Saeed and Shaker 2008); and Chad of Chad (Akan et al. 2012). Reports of heavy metal contamination in rivers that drain into Lake Chilwa in Malawi are also available (Saka 2006; Chidya et al. 2011; Ullberg 2015). On the other hand, studies on heavy metal contamination in Lake Chilwa are very rare. As such, this study was conducted with the main aim of assessing heavy metals (lead, cadmium, manganese, copper, zinc and iron) in Lake Chilwa. The choice of the heavy metals was dependent on those that were previously studied in the various rivers draining into the lake. This is in addition to risk assessment evaluation as regards the safety of the fish from the lake. It has to be noted that continuous heavy metal (which may bioaccumulate in fish) monitoring in fish is important because of the importance of fish as a source of food to the general human population (Rajeshkumar and Xi 2018; Hashim et al. 2014). On the other hand, monitoring of heavy metals in water is important because living organisms (fish, plankton and human beings among others) get exposed to the metals from uptake of water. Heavy metal monitoring in sediments is also very crucial because these store pollutants which may circulate back into the water column years after they were released. Additionally, it has to be emphasized that data on water quality monitoring in low- and middle-income countries are very

rare (Crocker and Bartram 2014). As such, any study on water quality-related issues in developing countries is very important not only for knowledge purposes but also for the safety of water (which is consumed) and aquatic organisms in these countries.

Materials and methods

Description of the study area

The study was conducted on the Zomba city side of Lake Chilwa in Malawi. Lake Chilwa (an endorheic lake) is spread across three districts in Malawi, namely Zomba, Machinga and Phalombe. Part of the lake forms a border between Malawi and Mozambique (Van-Zegreen and Munyenembe 1998). The Lake Chilwa is the second largest in Malawi and lies at 35°45'E and 15°15'S (Ratcliffe 1971). Lake Chilwa is about 40 km from north to south and 30 km from west to east. It is an inland drainage basin lake, with a depth of less than 5 m (van-Zegreen and Munyenembe 1998). The lake has an open water area of around 678 km², surrounded by about 600 km² of *Typha* swamps, 390 km² of marshes and 580 km² of seasonally inundated grassland of floodplain (Lake Chilwa Wetland Project 1999). Its salinity varies from 1 to 1.5 ppt with maximum levels reaching up to 10–15 ppt when most of the water evaporates (due to drought) and the depth and width of the lake waters shrink (Njaya et al. 2011). Although the salinity seems to be on the higher side (hence giving the water a salty taste), people from the area around the lake still uses its waters for drinking without even proper treatment (Khonje et al. 2012). The lake has been a Ramsar site (a wetland of international importance) in 1997.

Rivers Domasi, Likangala, Thondwe, Namadzi and Phalombe drain into Lake Chilwa (Wetlands International 2011). A large proportion of fish (25–30%) is caught from the lake (Njaya 2001) and is sold in Zomba city and surrounding areas.

In order to assess the spatial variation of water quality, the study purposively selected five sampling sites (as shown in Fig. 1), namely Bonga, Chaone, Thunde, Mchenga and Kachulu. Bonga is an area where Likangala River joins Lake Chilwa. Chaone is an area where there are human settlements on Chisi Island. Thunde, which is located on the other side of Chisi Island, has less human activity. Farming activities are dominant at Mchenga which is on the shores of the mainland. Human activities (fishing, water transportation and fish trade) are mostly done at Kachulu which is a harbour located close to the mainland. The choice of all these sites was dependent on the various human activities that happen in these areas.



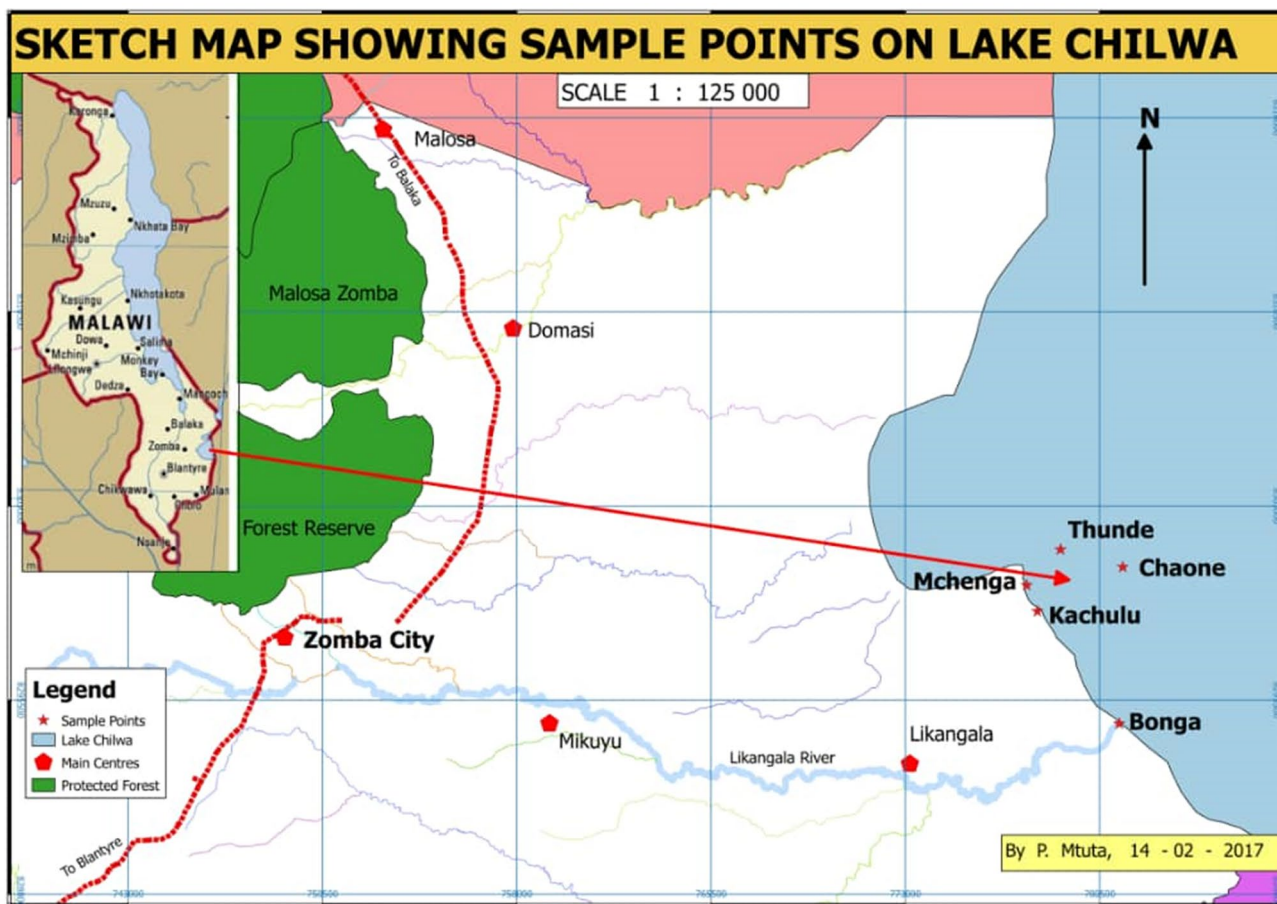


Fig. 1 Map showing study area

Chemicals and instruments used

In this study, sodium salicylate (99.8% purity), hydrogen peroxide (35% purity) and heavy metal standards (Pb, Cd, Mn, Cu, Zn and Fe) (99.9% purity) were obtained from Saarchem (Pty) Limited (South Africa); sodium hydroxide (99.8% purity) was obtained from Biotech Limited (India); ascorbic acid (99.8% purity) and nitric acid (55% purity) were obtained from Glassworld (South Africa).

The main instruments used were: standard portable meters (pH meter Wagtech International WE 30200 and electrical conductivity meter Hatch model MP4) and atomic absorption spectrophotometer (AAS, model GBC932). The method used for pH, electrical conductivity and total dissolved solids was electrometric, i.e. pH meter, conductivity meter and total dissolved solids meter methods, respectively.

Water sample collection

Standard methods from the American Public Health Association (APHA) (2005) and Malawi Bureau of Standards (MBS 2002) were used to collect water samples from five

sampling sites in both dry (November 2016) and rainy (March 2017) seasons. The water samples ($n = 40$) were collected using grab sampling technique at a depth of about 0.3 m below the surface of the lake into 10% HCl pre-cleaned 1 litre polystyrene bottles. To those samples where heavy metals were to be analysed, 1% nitric acid was added. All samples were collected in triplicate. Temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) were determined on site using standard portable meters (pH meter Wagtech International WE 30200 and Electrical conductivity meter Hatch model MP4). Stored in a cooler box, water samples were immediately transported to the chemistry laboratory of Physics and Biochemical Sciences Department, University of Malawi, The Polytechnic, for analysis.

Sediment sample collection

The method Osman and Kloas (2010) was used in the collection of sediment samples. The study used divers to collect bottom sediments (1–2 cm at the lake bottom) of the lake using an Eckman grab at a depth of 1–2 cm from the bottom of the lake. The collected sediments were transferred into



ziplock bags. The mean moisture content of the sediments was 11.3% which was similar to a study by Kaonga et al. (2015). Although it took 3 h to transport the sediments to the laboratory, the use of ziplock bags prevented any loss in moisture in transit. The sediments were transported to the laboratory in a cooler box.

Fish sample collection

According to Portt et al. (2006), the most commonly used fishing gear types used in surveys and research are gill nets, beach seines, hoop, fyke and trap nets and electrofishing among others. In this study fresh fish samples were collected directly from fishermen at the lake in both seasons (dry and rainy seasons). These fishermen use either gill nets or beach seines. Only fish caught on the same day of sampling were picked for the study. The sampling technique used was purposive. The study targeted common fish samples found in the lake which are: *Barbus paludinosus*, *Clarias gariepinus* and *Oreochromis shiranus chilwae*. Except for *B. paludinosus* which was collected in bulk due to its size, a minimum of three fish each were collected for *C. gariepinus* and *O. shiranus chilwae* in each of the seasons. The fish samples were also placed in sealed ziplock bags (which prevented any moisture loss) and it took approximately 3 h to transport them to the laboratory. The fish samples were transported in a cooler box filled with ice packs. Upon arrival at the laboratory, the samples were kept frozen in a freezer at $-20\text{ }^{\circ}\text{C}$ pending analysis.

Analytical methods

Heavy metals were determined in all the samples. On the other hand, pH, electrical conductivity, total dissolved solids, nitrates and phosphates were analysed in water samples only. All the laboratory work followed prescribed standard methods as explained in the next sections.

Nitrate determination

Nitrate (NO_3^-) was determined by reacting it with sodium salicylate under highly acidic conditions (APHA 2005). The addition of excess sodium hydroxide solution produced the sodium salt of the organic nitro complex. The nitro compound was soluble in water and produced a strong yellow solution. The intensity of the colour was proportional to the amount of nitrate in the sample and was measured at 410 nm on a spectrophotometer. The quantitative results were correspondingly obtained from the prepared standard calibration curve.

Phosphate determination

Phosphate (PO_4^{3-}) in water samples was determined by ascorbic acid method (APHA 2005). Measurements were taken with the aid of UV/Vis spectrophotometer (Spectronic 20 model) at 880 nm wavelength. The quantitative results were inferred from the standard calibration curve.

Determination of heavy metals in water samples

Using prescribed protocols in APHA (2005), all the water samples for metal analysis were digested using 5 mL concentrated nitric acid (analytical reagent, AR) to 50 mL of water sample in a 100-mL volumetric flask. And then, the mixture was heated on a hot plate to boil until the volume reduced to 20 mL. Another 5 mL of concentrated nitric acid was added and then heated for 10 min and allowed to cool. The solution was filtered and then diluted to the mark with distilled water in a 50-ml volumetric flask. The atomic absorption spectrophotometer (AAS, model GBC932) was used to quantitatively measure the heavy metals (Pb at 283.3 nm, Cd at 228.8 nm, Mn at 279.5 nm, Cu at 324.8 nm, Zn at 213.9 nm and Fe at 248.3 nm). Respective working solutions were prepared using standard reagents and run for inference. The detection limits for Cd, Cu, Fe, Pb, Mn and Zn were 0.001 $\mu\text{g/L}$, 0.003 $\mu\text{g/L}$, 0.0006 $\mu\text{g/L}$, 0.002 $\mu\text{g/L}$, 0.004 $\mu\text{g/L}$ and 0.001 $\mu\text{g/L}$, respectively.

Determination of heavy metals in sediment samples

Sediment samples were thawed at room temperature ($25\text{ }^{\circ}\text{C}$) and put in beakers. The samples were then oven-dried at $50\text{ }^{\circ}\text{C}$ until a constant weight was reached. A porcelain mortar and pestle were used to grind the sediment samples. The ground samples were then sieved using a 2-mm mesh plastic sieve. 2 g of sediments from each sample were weighed into nitric acid-cleaned beakers. The weighed samples were then digested using 5 mL concentrated nitric acid (AR) and few drops of 30% hydrogen peroxide (H_2O_2). The digested samples were filtered using filter paper into a 50-mL volumetric flask and filled up to the mark with distilled water. AAS was used to determine the heavy metals in the sample according to APHA (2005) protocol. The detection limits for Cd, Cu, Fe, Pb, Mn and Zn were 0.004 $\mu\text{g/g}$ dry weight (dw), 0.0003 $\mu\text{g/g}$ dw, 0.0001 $\mu\text{g/g}$ dw, 0.003 $\mu\text{g/g}$ dw, 0.002 $\mu\text{g/g}$ dw and 0.004 $\mu\text{g/g}$ dw, respectively.

Determination of heavy metals in fish samples

Frozen fish samples (whole fish) were thawed before being cut into small pieces using a plastic knife (to avoid metal contamination). The pieces were then put in acid-cleaned oven-dried crucibles. The samples were put in an oven set



at 50 °C to dry until a constant weight was reached. The dried samples were allowed to cool in a desiccator to avoid absorption of any moisture from the environment. The cooled fish samples were slightly ground using a porcelain mortar and pestle before being crushed into powdered form using a Nima magic blender. Next 2 g of the powdery fish samples was weighed on an electronic balance and the samples were then transferred into a clean beaker.

The samples for each fish species were digested in triplicates (APHA 2005). 18 mL of concentrated nitric acid was then added to each sample and heated on a hot plate at 100 °C in a fume hood chamber. A few drops of 30% hydrogen peroxide (AR) were added until there were no brown fumes. The fish sample solution from digestion process was then filtered into a 25-mL volumetric flask and filled to the mark with distilled water. The filtrate was then put into pre-acid-cleaned plastic bottles. The filtrates were then analysed for heavy metals using an AAS. The detection limits for Cd, Cu, Fe, Pb, Mn and Zn were 0.002 µg/g dry weight (dw), 0.003 µg/g dw, 0.002 µg/g dw, 0.001 µg/g dw, 0.005 µg/g dw and 0.001 µg/g dw, respectively.

Health risk assessment

The health risk assessment was estimated through the target hazard quotient (THQ) as described by Keshavarzi et al. (2018) with a minor modification. The THQ is an indication of the risk one gets when exposed to a pollutant (United States Environmental Protection Agency 2017). Values above unity indicate significant chronic toxic risk. THQ is estimated from the equation below:

$$\text{THQ} = \frac{\text{EF} \times \text{ED} \times \text{FIR} \times \text{CF} \times \text{CM}}{\text{WAB} \times \text{ATn} \times \text{RfD}} \times 10^{-3} \quad (1)$$

where THQ is the target hazard quotient, EF is the exposure frequency (365 days/year) (Ahmed et al. 2015) and ED is the exposure duration (70 years for non-cancer risk as

used by the USEPA 2011). FIR is the fish ingestion rate (29.3 g/person/day, Government of Malawi 2017), CF is the conversion factor (0.2) to convert fresh weight (Fw) to dry weight (Dw) in the event that the data are reported in fresh weight (El-Moselhy et al. 2014), CM is the fish heavy metal concentration (mg/kg dw), WAB is the average body weight (63 kg) (Msyamboza et al. 2013), ATn is the average exposure time for non-carcinogens (EF × ED) as used in characterizing non-cancer risk and RfD is the reference dose of the metal according to USEPA (2017) with values being 1×10^{-3} mg/kg/day for Cd, 4.0×10^{-2} mg/kg/day for Cu, 7.0×10^{-1} mg/kg/day for Fe, 1.4×10^{-2} mg/kg/day for Mn and 3.0×10^{-1} mg/kg/day for Zn.

Data analysis

IBM-SPSS Statistics version 20 software was used to analyse the data. *T* test was used to observe the variations among the sample means and between the sample types, respectively, at 95% confidence interval. Furthermore, Pearson (*r*) correlation examined the relationship between the levels of analytes in water, sediment and fish samples. Correlation analysis was also used to examine the relationship between heavy metals and other physico-chemical parameters.

Results and discussion

Physico-chemical parameters in water

Water pH

The mean water pH values in Lake Chilwa for the five sampling sites are shown in Table 1. Highest pH levels were recorded in dry season as compared to the rainy season. This is attributed to both run-off and rainfall which often times tend to be acidic (Peña et al. 2001). Thunde recorded

Table 1 Results of heavy metals and physico-chemical parameters in water samples

Parameter	Bonga		Chaone		Thunde		Mchenga		Kachulu		Min	Max	WHO	MS
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS				
pH	8.570	6.937	9.360	9.233	9.700	9.437	9.333	8.587	9.433	8.747	6.937	9.70	6.5–8.5	5.0–9.5
Temp (°C)	32.53	30.70	33.77	31.70	32.10	31.70	33.23	32.83	33.73	32.60	30.70	33.77		
TDS (mg/L)	2064	77	1948	2047	2045	1818	2158	1272	2119	1657	77	2119	1000	450–1000
EC (µS/cm)	2808	123	2701	2777	2814	2493	2936	1788	2878	2300	123	2936	700	700–1500
NO ₃ (mg/L)	0.632	2.033	1.084	2.166	0.865	5.290	0.896	6.565	3.201	0.388	0.388	6.565	50	6.0–10
PO ₄ (mg/L)	0.336	0.249	0.288	1.107	0.270	1.209	0.321	0.945	0.233	1.274	0.233	1.274	0.1	
Cd (mg/L)	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.002	n.d	n.d	0.002	0.003	
Fe (mg/L)	4.596	1.368	4.070	2.140	5.123	3.544	4.246	8.807	6.00	3.544	1.368	8.807	0.3	
Zn (mg/L)	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2.308	n.d	2.308	0.1	

DS dry season, RS rainy season, n.d not detected, MS Malawi Standards, WHO World Health Organization



the highest levels of pH for dry (9.7 ± 0.1) and rainy seasons (9.4 ± 0.01), while Bonga had the lowest for dry season (8.6 ± 0.01) and rainy season (6.9 ± 0.01). There were significant differences in mean pH values among the five sites for both seasons ($p < 0.05$). The pH found in this study is deemed good for fish production. According to Das and Nandi (2004), a pH of between 6.5 and 9.0 supports fisheries as it has a direct effect on fish growth apart from encouraging growth and survival of fish food.

In both seasons, all the sampling sites but Bonga in rainy season were not within the WHO acceptable pH drinking water values (pH 6.5–8.5) (WHO 2011). On the other hand, all the sampling sites except Thunde (pH 9.7) in the dry season were within the Malawi Standards drinking water values (pH 5.0–9.5) (MSB 2005). The possible reason for having slightly low pH at Bonga could be because the site is an inlet of Likangala River to Lake Chilwa where depositions of organic materials could occur. Likangala River receives wastewater effluent before it flows into Lake Chilwa. With time, the organic substances decompose and release carbon dioxide (CO₂) which combines with water to produce carbonic acid which decreases the pH of water. The importance of pH on the availability of metals in the water column and their release from sediments is well known. According to Atkinson et al. (2007), metals from sediments are released based on mostly the levels of pH in the water column above the sediments. Low pH levels encourage release of metals more than high pH levels. This means that the lowest pH of 5.0 found in this study could encourage the release of metals from sediments into the water column in the study area. The maximum pH (9.7) found in this study was higher than that found by Pathania et al. (2010) (8.4) in a fish pond located in Jalandhar, Punjab.

Total dissolved solids (TDS) in water

The mean concentration of total dissolved solids (TDS) for the five sampling sites in Lake Chilwa is shown in Table 1. The mean concentration of total dissolved solids (TDS) for four sampling sites (Bonga, Thunde, Mchenga and Kachulu) was higher in dry season than in rainy season. This could be attributed to low water levels in dry season that lead to an increase in the concentration of dissolved solids. On the other hand, in rainy season the water levels were high and there was dilution effect on total dissolved solids. Mchenga recorded the highest TDS value (2158 ± 1.15 mg/L), while Chaone recorded the lowest (1948 ± 1.53 mg/L) in the dry season. This could be attributed to settlement of minerals that failed to dissolve due to calmness of water leaving the water column with less concentration of TDS. The value of TDS is based on the availability of organic salts and elements in the water column (USEPA 2012). In the rainy season, Chaone recorded the highest TDS (2047 ± 0.58 mg/L), while Bonga

had the lowest (77 ± 0.02 mg/L). The reason for having very low TDS levels at Bonga in rainy season could be attributed to large volumes of water that were continuously flowing into the lake from Likangala River that reduced the concentration of dissolved solids at the site. The changes in TDS levels in surface water bodies are dependent on the effluent load, water balance (inflows and outflows) or cases of salt water intrusions (Weber-Scannell and Duffy 2007).

There were significant differences in the mean total dissolved solids among five sites for both seasons ($p < 0.05$). The study indicated that all the sites but Bonga in the rainy season were above the Malawi Standards drinking water values for TDS (450–1000 mg/L) (MSB 2005). On the other hand, the maximum TDS value (376 mg/L) reported by Pathania et al. (2010) in a fish pond located in Jalandhar, Punjab, was lower than the maximum found in Lake Chilwa (2119 mg/L) which is attributed to the fact that the lake is an inland drainage basin; as such, salts tend to accumulate in it.

Electrical conductivity (EC) of the lake water

The mean concentration of electrical conductivity (EC) for the five sampling sites in Lake Chilwa is shown in Table 1. The mean EC for the four sampling sites was higher in dry season than in rainy season. The possible reason could be attributed to low water dilution in dry season as both the incoming water levels are low due to less or no precipitation. On the other hand, in rainy season the water levels were high and there was dilution effect on ions. Mchenga recorded the highest EC (2936 ± 1.53 μ S/cm) and Chaone recorded the lowest (2701 ± 0.58 μ S/cm) in the dry season. In the rainy season, Chaone recorded the highest EC (2777 ± 1.00 μ S/cm), while Bonga had the lowest (123 ± 0.06 μ S/cm). The pattern of having high concentration of EC and other parameters in dry season as compared to rainy season has also been reported elsewhere. For example, a study done by Kumari et al. (2019) in Motia Lake in India found that the concentration of pH, EC, NO₃ and PO₄ was higher in pre-monsoon (before the rains) than during monsoon time (rainy season).

The highest recording of EC in rainy season at Chaone could be as a result of weathered rock material from Chisi Island where Chaone is located. The rock material could be carried down the lake by surface run-off. In a study done by Garson (1960) on Chisi Island, it was found that the area has various rock minerals including carbonatites and manganese oxides. It is well known that if there are many minerals in the water, the ability of that water to conduct electric current is high Mushatq et al. (2013), hence high EC. Although a stream that is a recipient of sewage effluent tends to have high EC levels (Daniel et al. 2002), in this study at Bonga (a point where Likangala River, which receives sewage effluent, drains into the lake) the levels were low. This is mainly

attributed to water volumes and distance from the point of discharge to the lake.

There were significant differences in the mean electrical conductivities among five sites for both seasons ($p < 0.05$). The study indicated that water from Bonga in the rainy season was the only site suitable for domestic use because the limit for EC for drinking and potable water set by WHO is 700 $\mu\text{S}/\text{cm}$ (WHO 2011) and 700–1500 $\mu\text{S}/\text{cm}$ according to the Malawi Standards (MSB 2005).

Nitrate levels in water for dry and rainy seasons

In the rainy season, the levels of nitrate in water samples ranged from 0.388 to 6.565 mg/L, while in dry season the range was 0.632–3.201 mg/L (Table 1). In both seasons, all the sampling sites had nitrate levels below the WHO drinking water standards (50 mg/L) (WHO 2011). On the other hand, Mchenga was the only site that had nitrate levels within Malawi drinking water standards (6.0–10 mg/L) (MSB 2005). The sources of nitrates in water samples could be the use of inorganic fertilizers and also wastewater effluent. The highest level of nitrate was observed in the dry season at Mchenga, while the lowest was at Kachulu in the same season. This could be attributed to irrigation farming that involves the use of fertilizers in the area around Mchenga as compared to Kachulu where people concentrate on fishing. The maximum level of nitrates found in this study was lower than the values found in Likangala River (maximum recorded was 57.59 mg/L) which feeds into Lake Chilwa in a study done by Chidya et al. (2011) which could be attributed to dilution. On the other hand, the maximum nitrate levels (6.6 mg/L) found in this study were higher than those reported by Pathania et al. (2010) in a fish pond (maximum 2 mg/L) located in Jalandhar, Punjab. The difference between the nitrate levels in the lake and the pond is attributed to variations in nutrient loads between the two locations.

The study indicated significantly higher levels of nitrates in water samples for rainy season than those of dry season ($p < 0.05$). The possible reason for increased levels of nitrates in rainy season could be the application of nitrogenous fertilizers in the upland farms that was transported down to the lake by surface run-off. Wastewater treatment plants effluents from Zomba municipal and Chancellor College that are discharged directly into Likangala River could also be the reason for high levels of nitrates. In a study by Njaya (2001), it was reported that Likangala River has an influence on the hydrochemistry of Lake Chilwa.

Phosphate levels in water samples for dry and rainy seasons

In the dry season, the levels of phosphate in water samples ranged from 0.233 to 0.336 mg L⁻¹, while in rainy season the range was 0.249–1.274 mg/L (Table 1). The sources of phosphates in water samples are the use of inorganic fertilizers and geology of the area. In Malawi, the major source of phosphates is igneous rocks (containing carbonatites and mica pyroxenites) which are also found in the Lake Chilwa basin (Garson 1962). This explains why the highest level of phosphates was observed in the rainy season at Kachulu sampling site (1.274 mg/L) which is a harbour. Furthermore, the higher phosphate levels at Kachulu could be attributed to the use of phosphorus detergents for washing clothes and uncontrollable disposal of wastes.

There were significantly higher levels of phosphates in water samples for rainy season than those of dry season ($p < 0.05$). This may be attributed to surface run-off from agriculture fields that were applied with inorganic fertilizers containing phosphates. It may also be caused by indiscriminate dumping of solid and liquid wastes since the area does not have a specific dumping site. It has to be noted that the other contributing factor of phosphates to a surface water body is wastewater. According to de-Bashan and Bashan (2004), wastewater is one of the major sources of phosphates. Phosphates are a limiting nutrient in that they are the main cause of eutrophication in all classes of surface water bodies. However, in this study, the highest quantities of phosphates were not detected at Bonga (where Likangala River joins Lake Chilwa) an indication that the major source of phosphates in Lake Chilwa was not wastewater. The maximum concentration (1.274 mg/L) of phosphate in Lake Chilwa was higher than the maximum concentration (0.301 mg/L) found by Pathania et al. (2010) in a fish pond located in Jalandhar, Punjab, an indication of different loading rates.

Concentration of heavy metals

Concentration of heavy metals in water and sediment for dry and rainy seasons

Only cadmium, iron and zinc were detected in water samples. (Results are shown in Table 1.) The results for sediment samples are presented in Table 2.

The study indicated the absence of lead in water and sediments for dry and rainy seasons. This was similar to a study by Karadede and Unlu (2000) in Ataturk Dam, Turkey, in which they did not detect lead in water, sediments and fish samples but copper, iron, manganese and zinc. The results for water samples did not concur with previous studies conducted in inland lakes that have been described in



Introduction section. As shown in Table 1, cadmium was only detected in water in the dry season at Kachulu sampling site. The levels in water for the dry season ranged from below detection limit to 0.002 mg/L. The concentration of cadmium in water samples was below the WHO drinking water standards (0.003 mg/L) (WHO 2011). There was no significant difference in the levels of cadmium in water samples between dry and rainy season ($p > 0.05$). The possible sources of cadmium at Kachulu which is a harbour were anthropogenic activities such as the use of phosphate fertilizers and burning of fossil fuels (Challa and Kumar 2009). The results were in line with a recent study on heavy metals conducted in Semarang, Indonesia, which suggested that low cadmium concentrations could come from natural sources or minor human activities (Almiqrhi 2018).

Manganese was undetected in water samples for both seasons. On the contrary, in the dry season the level of manganese in sediments ranged from 4.788 to 9.775 mg/kg, while in the rainy season the range was 2.253–10.656 mg/kg (Table 2). There was no significant difference in concentration of manganese in sediment samples between dry season and rainy season ($p > 0.05$) at Thunde site. The possible sources of manganese in sediments are salts and mineral precipitates commonly spread on the floors of lakes (Damodharan 2013), and this perhaps explains the presence of Mn in the sediments.

Copper was not detected in water samples for both seasons. On the other hand, in the dry season the level

of copper in sediments ranged from 0.249 to 1.273 mg/kg, while in the rainy season it ranged from below detection limit to 1.629 mg/kg (Table 3). The concentration of copper was significantly higher in dry season than in rainy season ($p < 0.050$). The source of copper pollution is mainly from extensive use of pesticides, metals and waste discharges (Michael 1986). This is worsened by the fact that copper is a food additive used in animal feeds (hence could be found in animal waste) apart from the fact that it is incorporated in fertilizers as a plant nutrient (Abbasi et al. 1998). Almost all these copper sources could have contributed to high copper levels detected in sediments at Bonga which is an inlet of Likangala River,

Zinc was not detected in water samples for dry and rainy seasons at Bonga, Chaone, Thunde and Mchenga sites, but the levels of the rainy season at Kachulu site were in the range of detection limit to 2.308 mg/L. The zinc concentration detected in the rainy season was above the WHO drinking water standards (0.1 mg/L) (WHO 2011). The possible sources of zinc in water in the rainy season could be surface run-off from semi-urban areas, leaching from fertilizers and burning of waste materials at Kachulu harbour which is the only place where it was detected in water samples. According to Damodharan (2013), zinc can find its way into water bodies through run-off (from agricultural and industrial areas) and waste effluent. In the dry season, the level of zinc in sediment samples from Lake Chilwa ranged from 0.153 to 1.825 mg/

Table 2 Results of heavy metals in sediment samples (mg/kg dry weight, dw, basis)

Parameter	Bonga		Chaone		Thunde		Mchenga		Kachulu		Min	Max
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS		
Mn	5.396	3.250	7.746	10.66	9.775	9.785	4.788	2.253	5.509	3.967	2.253	10.66
Cu	1.273	1.629	0.575	0.000	0.637	0.000	0.249	0.000	0.548	0.405	0.000	1.629
Zn	1.659	1.527	1.078	0.209	1.825	0.245	0.153	1.086	1.289	0.000	0.000	1.825
Fe	392.3	445.9	282.8	376.2	357.4	371.6	156.5	232.7	235.3	307.2	156.5	445.9

DS dry season, RS rainy season

Table 3 Results of heavy metals in fish samples (mg/kg dry weight, dw, basis)

Fish type	Cd		Mn		Cu		Zn		Fe	
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS
<i>O. shiranus chilwae</i>	n.d	0.003	0.246	0.065	0.406	0.544	2.078	4.815	18.64	18.63
<i>C. gariepinus</i>	n.d	0.003	0.467	1.178	0.406	0.917	2.214	1.712	32.31	9.683
<i>B. paludinosus</i>	n.d	0.006	0.015	0.206	0.416	0.683	2.004	2.698	16.34	11.78
Min	–	0.003	0.015	0.065	0.406	0.544	2.004	1.712	16.34	9.683
Max	–	0.006	0.467	1.178	0.416	0.917	2.214	4.815	32.31	11.78
Overall Mean	–	0.004	0.243	0.483	0.409	0.715	2.099	3.075	22.42	13.37
FAO/WHO	0.1		2–9		3		60		43	

n.d not detected

kg, while in the rainy season the range was from below detection to 1.525 mg/kg (Table 3). There was a significantly higher concentration of zinc in dry season than in rainy season ($p < 0.05$). Zinc levels in sediments were high in dry season possibly because in the rainy season there was churning effect in the lake that could uplift the sediments, thereby leaving the metal ions in suspension. The possible sources of zinc in sediments were waste discharges and agricultural field run-off (mainly from fertilizers containing zinc) among others (Lew 2008). Data obtained were lower than that found by Mahamat et al. (2017) for sediment samples obtained in Léré Lake, Chad.

The results at Kachulu showed a notable switch of the presence of zinc between water and sediment samples in both seasons as zinc was detected in water in the rainy season only and in sediments in the dry season only. This may be attributed to the complete deposition of sediments in dry season when water was calm before being remobilized back to water due to the churning effect of rain. It is a well-known fact that sediments have a capacity for more heavy metal accumulation with time and remobilize them back to water and the food chain. According to Aderinola et al. (2009), sediments tend to hoard metals; as such, these contaminants may be absent in the water column but are present in them. Sediments can have high concentration of both metals and other pollutants (like organic substances) (Singovszka et al. 2017).

Iron in water samples ranged from 4.07 to 6.0 mg/L in the dry season, while in rainy season the range was 1.368–8.807 mg/L. In all the sampling sites, iron levels were above the WHO (0.3 mg/L) drinking water standards (WHO 2011). The presence of iron in the waters of Lake Chilwa could be attributed to the discharges of iron containing wastes produced in Zomba city and Kachulu Trading Center. The range of iron concentration in sediment samples in Lake Chilwa for the dry season was 156.53–392.32 mg/kg, while in the rainy season it was 232.67–445.93 mg/kg (Table 3). There were significantly higher levels of iron in rainy season than in dry season ($p < 0.05$). The results were lower compared to Aderinola et al. (2009), where the average concentration of iron in sediments was 482 mg/kg. However, there was a similar trend to the present study where both recorded highest concentration of iron in sediments, followed by fish then water.

The highest concentration of iron in sediments was at Bonga which is an inlet from Likangala River. This may be as a result of the accumulation of sediments that contain iron elements originating from the inhabitants along the Likangala River. In accordance with Almiqrhi (2018), a tidal stream can cause heavy metals dissolves in water to get adsorbed at a river mouth.

The source of heavy metals in the water column therefore can be attributed to direct run-off from land into the lake,

metal loads from the rivers draining into the lake and recirculation of metals from sediments in the event of waves. According to Kuriata-Potasznik et al. (2016), rivers flowing into a lake are one of the key factors as regards the input of heavy metals in the water body.

Levels of heavy metals in fish

The study also analysed the samples of three different species of fish for the possible presence of heavy metals, namely lead (Pb), cadmium (Cd), manganese (Mn), copper (Cu), zinc (Zn) and iron (Fe). The results of different fish samples, namely *Barbus paludinosus*, *Clarias gariepinus* and *Oreochromis shiranus chilwae*, are presented in Table 3.

Lead was not detected in fish samples. Fish samples for the rainy season showed the presence of cadmium ranging from below detection limit to 0.006 mg/kg (Table 3). The levels of cadmium in fish samples were below the maximum limit for the FAO/WHO standards for cadmium in fish for consumption (0.1 mg/kg) (FAO/WHO 1999). *B. paludinosus* recorded high levels of cadmium than the other two species. This may imply that *B. paludinosus* has more potential for accumulating cadmium metal than other species, possibly because of its feeding habit. *B. paludinosus* has an omnivorous habit. A study conducted by Dadebo et al. (2013) in Lake Ziway, Ethiopia, revealed that the feed of *B. paludinosus* varies depending on season. In both seasons (dry and rainy), it feeds on insects and detritus. On the other hand, zooplankton is fed mainly in the dry season, while phytoplankton is fed in the wet season.

In the dry season, manganese level in fish samples ranged from 0.015 to 0.467 mg/kg. In the rainy season, manganese concentration ranged from 0.065 to 1.178 mg/kg (Table 3). In both seasons, the levels of manganese in fish were below the FAO/WHO standards (2–9 mg/kg) (FAO/WHO 1999). The concentration of manganese in fish samples was significantly higher in rainy season than in dry season ($p < 0.05$). In both seasons, *C. gariepinus* recorded highest levels of manganese (0.467 mg/kg for dry season and 1.177 mg/kg for rainy season). There are various anthropogenic sources of manganese, which include fertilizers and pesticides. Manganese tends to bioconcentrate in bottom feeding organisms including some fish (Abbasi et al. 1998).

In the dry season, copper levels in fish samples ranged from 0.406 to 0.416 mg/kg. In the rainy season, fish samples had copper ranging from 0.544 to 0.917 mg/kg (Table 3). In both seasons, the concentration of copper in fish samples was below the FAO/WHO standards for copper in fish for consumption (3 mg/kg) (FAO/WHO 1999). Paired *t* test revealed that copper levels in fish samples were significantly higher in rainy season than in dry season ($p < 0.05$). This could be attributed to higher levels of copper found in the



sediments in the rainy season that were consumed as detritus together with zooplankton and phytoplankton. *C. gariepinus* recorded a higher concentration of copper (0.917 mg/kg) than *Barbus* and *Oreochromis* species. This may indicate that *C. gariepinus* has more potential of accumulating copper metals than the two species. The possible reason could be the habitat for *C. gariepinus*. The fish species usually live and feed on living organism and detritus found in the mud which is the major constituents of sediments. *C. gariepinus* is mostly active at night, has multiple food sources (both living and dead matter), and dwells in mud where it survives the seasons (Anoop et al. 2009).

In the dry season, zinc levels in fish samples ranged from 2.004 to 2.214 mg/kg. In the rainy season, zinc ranged from 1.712 to 4.815 mg/kg (Table 3). In both seasons, the concentration of zinc in fish samples was below the FAO/WHO standards for zinc in fish for consumption (60 mg/kg) (FAO/WHO 1999). The concentration of zinc in the fish samples for rainy season was significantly higher than in dry season ($p < 0.05$). Zinc in fish samples can originate from both food and water and eventually it accumulates in the organs of the fish (Fazio et al. 2014; Sfakianakis et al. 2015). *O. shiranus chilwae* had the highest levels of zinc in the rainy season than the other species. In this study, the zinc levels were higher than those of copper which was also the case in a study done in Poland in fish species by Łuczyńska et al. (2018).

Iron levels in fish samples ranged from 16.342 to 32.314 mg kg⁻¹ in dry season. In the rainy season, iron ranged from 9.683 to 18.631 mg/kg (Table 4). In both seasons, the concentration of iron in fish samples was below the FAO/WHO standards for iron in fish for consumption (43 mg/kg) (FAO/WHO 1999). Iron levels in dry season were significantly higher than those in rainy season ($p < 0.05$).

Target hazard quotient (THQ) values of heavy metals in fish samples

The THQ values are shown in Table 4. The ranges of THQ values in dry season (DS) and rainy season (RS) were: Cd (RS: 0.001–0.004); Mn (DS: 0.001–0.008), (RS: 0.002–0.04); Cu (DS: 0.005–0.005), (RS: 0.006–0.010); Zn (DS: 0.003–0.007), (RS: 0.003–0.007); and Fe (DS:

0.540–1.073), (RS: 0.320–0.620). The values were generally lower than unity which shows that based on heavy metals analysed, the fish is safe for consumption. *C. gariepinus* had a higher THQ for iron in the dry season possibly because it feeds on dead animal matter as it survives in shallow mud for a long period of time (Anoop et al. 2009). The THQ values found under this study were in the same ranges as those found by Yi et al. (2011) (assessed heavy metals in fishes in the middle and lower reaches of the Yangtze River basin), Kesharvazi et al. (2018) (assessed three fish species from the Persian Gulf) and Orosun et al. (2016) (assessed fish species from Kiri Dam and River Gongola, north-eastern Nigeria). On the other hand, these values were lower than those found by Sharif et al. (2016) (analysed shell fish from Kudat, Sabah, Malaysia). The lower values found in this study as compared to those found in the Malaysian study are attributed to species differences. It is a well-known fact that shell fish tend to have high pollutant levels than other fish species due to their feeding habit as they mostly feed on detritus and mud.

Correlation and paired t test analysis of heavy metals in water, sediments and fish

There was a strong negative correlation of manganese levels in sediments and fish samples for both rainy and dry seasons ($r = -1.00$). The possible reason could be that many types of fish rely on a wide variety of feed such as zooplankton and phytoplankton than detritus (which forms a larger part of sediments that bind metals) which in dry season is mostly only available to benthic fishes due to calmness of the lake.

Similarly, there was a strong positive correlation of copper levels in sediments and fish samples for rainy season ($r = 0.93$). This could be attributed to the churning effect of rains that renders the suspension of detritus to be readily available for feed to both benthic and pelagic fish. In the dry season, copper in sediments and fish samples was not strongly correlated ($r = -0.37$). Zinc in sediments and water samples for rainy season was not strongly correlated ($r = -0.52$). The possible reason could be the binding of metals to sediments as they settled to the bottom of the lake. Antagonistically, sediments may release more metal elements in water due to churning effect of the rains/wind. Furthermore, zinc levels in sediments and fish samples for the

Table 4 Target hazard quotient (THQ) of heavy metals in the fish species

Fish type	Cd		Mn		Cu		Zn		Fe	
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS
<i>O. shiranus chilwae</i>	–	0.001	0.008	0.002	0.005	0.006	0.003	0.007	0.620	0.620
<i>C. gariepinus</i>	–	0.001	0.002	0.040	0.005	0.010	0.003	0.003	1.073	0.320
<i>B. paludinosus</i>	–	0.004	0.001	0.007	0.005	0.008	0.003	0.004	0.540	0.390



dry season were not strongly correlated ($r = -0.05$). In addition to that, there was a strong negative correlation of zinc in sediments and fish samples for rainy season ($r = -0.76$). The possible reason could be the tossing of waves (swash–backwash) (Hanamgond et al. 1999) which helps in the release of metals from sediments so that they become available in the water column where they can be picked by pelagic.

There was a strong negative correlation of iron in sediments and water samples for dry season ($r = -0.79$). This negative correlation indicated that as the levels of iron in sediments were increasing, the levels in water decreased. This could be attributed to the calmness of the lake during dry season which allows the metals to settle down together with sediments. On the other hand, iron in water and fish samples for rainy season was not strongly correlated ($r = -0.47$). Contrary, there was a strong correlation of iron levels in sediments and fish samples for the dry season ($r = 0.65$). Also, there was a strong negative correlation of iron levels in sediments and fish samples for the rainy season ($r = -0.64$). The possible reason could be that fish relied on a wide range of feed than detritus.

Relationship of heavy metal concentrations in water to other physico-chemical parameters

There was a strong negative correlation between cadmium and nitrate in water for the dry season ($r = -0.60$) at Kachulu site. The reason is that cadmium reacts with nitrates to produce nitrites (Margeson et al. 1980). Therefore, the levels of nitrates were reduced in the presence of cadmium at Kachulu site. Similarly, there was a strong correlation between cadmium and phosphate in water for the dry season at Kachulu site ($r = 0.69$). The reason is that phosphate rocks (which are used in fertilizer production) contain certain levels of cadmium. According to Roberts (2014), phosphorus fertilizers contain cadmium.

Likewise, a strong correlation existed between cadmium and pH in water for the dry season at Kachulu site ($r = 0.62$). On the other hand, cadmium and electrical conductivity in water for dry season were not strongly correlated at Kachulu site ($r = 0.19$). Similarly, cadmium and total dissolved solids in water for dry season were not strongly correlated at Kachulu site ($r = 0.17$). Also cadmium and temperature of water for dry season were not strongly correlated at Kachulu site ($r = -0.19$).

There was a strong negative correlation between zinc and nitrates in water for the rainy season at Kachulu site ($r = -0.64$). On the other hand, zinc and phosphates in water for rainy season were not strong correlated at Kachulu site ($r = 0.43$). Similarly, zinc and pH in water for rainy season were not strong correlated at Kachulu site ($r = 0.09$). The analysis also revealed that zinc and electrical conductivity in water were also not strongly correlated at Kachulu site

($r = 0.21$). Likewise, zinc and total dissolved solids in water were also not strongly correlated ($r = 0.2$). Equally, zinc and temperature in water were also not strongly correlated at Kachulu site ($r = 0.45$).

Pearson correlation showed that iron and physico-chemical parameters were not strongly correlated. These are: iron and nitrate in water for both dry and rainy seasons: $r = -0.03$ and $r = -0.37$, respectively; iron and phosphates in water for the dry season and rainy season: $r = 0.08$ and $r = 0.31$, respectively; and iron and pH in water for the dry season and rainy season: $r = 0.33$ and $r = 0.09$, respectively.

On the other hand, there was a strong correlation between iron and electrical conductivity in water for dry season ($r = 0.75$). In the rainy season, iron and electrical conductivity in water were not strongly correlated ($r = 0.11$). Similarly, there was a strong correlation between iron and total dissolved solids in water for dry season ($r = 0.68$). This could possibly be as a result of metal accumulation in reduced volume of water since metals such as iron are the components of TDS in water. In the rainy season, iron and total dissolved solids in water were not strongly correlated ($r = 0.11$). Also, iron and temperature of water for dry season were not strongly correlated ($r = 0.12$). In the rainy season, iron and temperature in water were also not strongly correlated ($r = 0.2$).

Conclusion

This study assessed heavy metals in water, sediments and fish from Lake Chilwa in Zomba, Malawi. The results showed that pH, EC and TDS levels were above the WHO and MBS limits for drinking water except for Bonga in rainy season. Nitrates were detected at all sites but were below the WHO drinking water standards. Phosphates were observed to be higher in the rainy season than in the dry season. The main sources of nitrates and phosphates into the lake are attributed to fertilizers are wastewater from the treatment plants.

The study revealed that the concentration of Pb, Mn and Cu was undetectable in the water. However, Cd and Zn were only detected at Kachulu in the dry and rainy season, respectively. Fe was the only metal detected in water at all the sites. It was observed that Fe and Zn were above the WHO drinking water standards, but the rest of the metals were below. Further observation showed higher levels of heavy metals in water in the rainy season than in dry season. Pb was not detected in sediments, while Mn, Cu and Zn were higher in the dry season than in rainy season except for Fe which displayed an opposite trend to the others.

All heavy metals were detected in fish samples except Pb but were within the WHO limits for human

consumption. The concentration of metals in fish was higher in the rainy season than in the dry season except for iron which showed an opposite trend. This study revealed that anthropogenic activities contributed to the elevation of heavy metals besides geogenic sources.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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