

POTENTIALLY TOXIC TRACE ELEMENTS IN MAHAWELI RIVER IN SRI LANKA DURING THE DRY SEASON

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ABSTRACT

Mahaweli river flows through seven districts in Sri Lanka and the river water could get contaminate with heavy metals and metalloids due to various reasons. Water samples collected from 15 locations (Hatton, Watawala, Ginigathhena, Nawalapitiya, Ualapane, Gampola, Geliyoa, Kandy, Manampitiya, Sungawila, Somawathiya, Mawil-aru Anicut, Seru Nuwara, Upparu Ferry and Ralkuli Ferry) were analyzed for potentially toxic trace elements, namely As, B, Cd, Cr, Cu, Pb, Mn, Hg, Ni, Tl and Se by using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The results were compared against the drinking-water standards set by the WHO. Mercury (Hg) and Tl were not recorded in the water samples. Lower reaches of rive Mahaweli from Peradeniya was comparatively more contaminated than the upper reaches. In Ralkuli Ferry and Upparu Ferry, the trace elements such as B ($25,012 \pm 3,446.5$ ppb and $19,867 \pm 4,991.5$ ppb, respectively), Cu ($10,211 \pm 1,079$ ppb and $8,251.9 \pm 3,862.80$ ppb, respectively), As (233.5 ± 26.7 ppb and 298.6 ± 44.7 ppb, respectively) and Se ($1,361.1 \pm 144.3$ ppb and $1,558.2 \pm 18.0$ ppb, respectively) were significantly higher than the other locations and exceed the WHO permissible levels.

Key Words: ICP-MS, Mahaweli River, Trace elements

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INTRODUCTION

Being the longest river in Sri Lanka, Mahaweli river runs for 333 km through seven districts of Badulla, Kandy, NuwaraEliya, Matale, Pollonnaruwa, Anuradhapura and Trincomalee. Twenty-five percent of the cultivated area, mainly tea, vegetable and paddy cultivations in Sri Lanka have been irrigated using Mahaweli water (Dissanayake *et al.*, 2007 and Aravinna *et al.*, 2015). Environmental pollution by trace elements could be due to various reasons such as fertilizer and pesticide use, atmospheric deposition, disposal of solid wastes, application of sewage and sludge, etc. (Gautam *et al.*, 2014). The prevalence of Chronic Kidney Disease of Unknown Etiology (CKDu) in the North Central Province (NCP) of Sri Lanka has been a major health issues in Sri Lanka (Dissanayake *et al.*, 2007 and Jayatilake *et al.*, 2013), which has often related to poor quality of drinking water.

Trace elements are naturally present in river water up to certain permissible extent. Even though Cd, As and Hg are extremely toxic, some heavy metals such as Cr, Mn, Co, Cu, Fe and Zn are essential in trace levels for bio-chemical processes of plants and animals. However, they also become toxic at higher concentrations (Dissanayake *et al.*, 1987 and Paul, 2017). Many researchers have described that there is an increase in heavy metal concentration in fishes and in edible aquatic plants owing to direct absorption (i.e. bio-concentration) from the increased levels of heavy metals in river water (Taymaz *et al.*, 1984; Clemens, 2006 and Indrajith *et al.*, 2008) and also bioaccumulation of heavy metals through foods (Le and Ngo, 2014 and Kananke *et al.*, 2016). Mahaweli river receives considerable fraction of total discharge from agricultural lands and urban areas (Dissanayake and Weerasooriya, 1986), and hence, there is a potential risk of distribution of trace metals from the upper catchment to its lower catchment. At lower pH levels, the uptake and the bio-availability of some heavy metals are increased. Organic matter in the soil may release heavy metals during their decomposition and the dissolved organic matter may increase the mobility and uptake of such heavy metals by aquatic plants and other aquatic fauna (Sivanantha *et al.*, 2016).

Therefore, our aim was to assess the current contamination status of few trace elements in the Mahaweli river water from the upper catchment to the lower catchment. Further, the study compared the trace element levels in Mahaweli river water with the

WHO potable water permissible levels (WHO, 2011; Table 1) to understand level of exposure of the human population to toxic trace elements.

MATERIALS AND METHODS

In this study, water samples were collected from 15 locations in Sri Lanka along the Mahaweli river water flow, i.e. Hatton, Watawala, Ginigathena, Nawalapitiya, Ualapane, Gampola, Gelioya, Kandy, Manampitiya, Sungawila, Somawathiya, Mawil-aru Anicut, Seru Nuwara, Upparu Ferry and Ralkuli Ferry during mid-April to Mid-May 2017. During this period no rain was prevailed in the study area. Samples were analyzed for heavy metals such as Boron (B), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), Thallium (Tl) and Selenium (Se), and for the metalloid Arsenic (As) by using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo Fisher Scientific CAQ Model, SN-03380R) at the Analytical Laboratory of the Office of the Registrar of Pesticides at Gatambe, Peradeniya, Sri Lanka. Elemental analysis was performed as per the laboratory-validated method using (AOAC Official Method 993.14; AOAC, 2012) and United States Environmental Protection Agency (U.S.EPA) Method 200.8 (U.S.EPA,1994).

Preparation of calibration standards

Multi-element calibration standards (working standards) were prepared using the standard multi-element stock solutions and nitric acid (4 %) according to the calibration ranges given in Table 1, and the calibration curves were prepared accordingly.

Table 1. Calibration range and limit of detection (LOD)

Element	Calibration range ($\mu\text{g/l}$)	LOD ($\mu\text{g/l}$)
Boron (B)	0.25 – 15.00	0.10
Chromium (Cr)	0.049 – 2.998	17.00
Manganese (Mn)	0.025 – 1.500	268.00
Nickel (Ni)	0.049 – 2.998	30.00
Copper (Cu)	0.049 – 2.998	0.10
Arsenic (As)	0.10 – 6.00	2.00
Selenium (Se)	0.25 – 15.00	38.00
Cadmium (Cd)	0.025 – 1.500	4.00
Mercury (Hg)	0.20 – 1.20	4.00
Thallium (Tl)	0.25 – 15.00	0.10
Lead (Pb)	0.10 – 6.00	186.00

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Sample analysis and quantification

Water samples (115) were collected into acid washed polypropylene bottles from 15 locations and pH of each sample was measured and adjusted to pH 2.0. Then samples were kept in a cool dark place until them subject to chemical analysis. One gram/ml from each collected sample was transferred into 100 ml volumetric flasks and diluted with 4 % HNO₃ acid. Samples were filtered with 0.25 µm filters and injected to the ICP-MS instrument (Thermo Fisher Scientific-German) in duplicates. Further dilutions were done accordingly.

Calculation of elemental concentration

Readings taken from the ICP-MS was calculated according to the equation in order to convert the instrument readings into SI units.

Eq. 1

$$\text{Concentration (mg/kg)} = \frac{\text{Instrumental concentration (mg/l)} \times \text{Sample Volume (ml)}}{\text{Sample weight (kg)}}$$

Note: Density of water was calculated as 1g/ml; sample concentration is declared as mg/l.

In order to maintain the precision and accuracy of the sample analysis, a blank and spiked sample was analyzed with other unknown samples at each batch of water sample analysis.

Standards for trace elements in potable and surface water

The study considered the standards set by different organizations (Table 2) such as WHO, EPA and SLSI (Sri Lanka Standards Institution). As there are no major differences in between drinking water and surface water standards, WHO Drinking Water Standard was used as the base for comparison of results in this study.

Table 2.The maximum levels of metalloid and heavy metals in potable and surface water, established by different organizations

Elements	Element Maximum concentrations for potable water($\mu\text{g/l}$)		Element maximum concentrations for surface water ($\mu\text{g/l}$) – Source: Surface Water Directive 1989 EPA regulation	
	WHO: 4 th edition (2011)	SLSI:614 (2013)	A1-Water is used as drinking water after purifications	A2- Bathing
As*	10.00	10.00	50.00	50.00
B	2400.00	-	2000.00	2000.00
Cd	3.00	3.00	5.00	5.00
Cr	50.00	50.00	50.00	50.00
Cu	2000.00	1000.00	50.00	100.00
Hg	6.00	1.00	1.00	1.00
Mn	400.00	100.00	50.00	300.00
Ni	70.00	20.00	-	-
Pb	10.00	10.00	50.00	50.00
Se	40.00	10.00	10.00	10.00
Tl	2.00	-		

*Refer to Table 1 for complete name

RESULTS AND DISCUSSION

The average concentrations of toxic trace elements analyzed in 115 water samples along Mahaweli river flow collected at different sampling locations are shown in Table 3. The pH values of the water showed an average of 6.60 ± 0.38 .

Hg and Tl

The results revealed that Hg and Tl contents in all samples are less than the LOD (Hg $4.00 \mu\text{g/l}$ and Tl $0.1 \mu\text{g/l}$) and consequently those levels are significantly lower than the relevant WHO drinking water permissible levels (Table 2). The results indicated that though most of the industries, hospitals and water treatment plants are established closer to the river systems and additional contaminants may get into water flow through some agricultural areas, etc., Hg and Tl contaminations are well-controlled in Sri Lanka, as reported in other countries (Le and Ngo, 2014).

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B and Cu

The LOD for both B and Cu are 0.1 µg/l. Almost all of the samples were contaminated with detectable levels of these two elements (Table 3; Figure 1). The data showed that the mean concentrations of two metals were within the range of 1.2-78.9 µg/l of B and 0.6-451.4 µg/l of Cu from Hatton to Seru Nuwara. All readings were below the WHO permissible levels (Table 2).

The water samples collected from Rulkuli Ferry to Upparu Ferry were highly contaminated with B (25,012.0 and 19,867.3 µg/l, respectively) and Cu (10,211.0 and 8,251.9 µg/l, respectively) and the water in both locations exceeded the WHO permissible levels (Table 2) of these two trace elements.

Cr, Ni, Se, Mn and As

Results of the study revealed that the water contamination of the heavy metals Cr, Ni, Se and Mn and the metalloid As in Mahaweli river from Hatton to Peradeniya were less than their respective LODs. The results of the upstream of the Mahaweli river agree with Illeperuma (2000) who reported that heavy metal concentrations at Kelani river were at or below 7.4 µg/l/Pb, 2.7 µg/l/Cd, 10.2 µg/l/Cu and 650 µg/l/Mn. Further, the mean values of water contamination from Cr, Ni, Se, Mn and As at the downstream locations from Manampitiya to Upparu Ferry are illustrated in Figure 2.

Table 3. Range of concentrations detected and mean concentrations ($\mu\text{g/l}$) of heavy metals and metalloids detected in Mahaweli riverat different locations

No.	Location	No. of samples taken	B ($\mu\text{g/l}$)			Cr ($\mu\text{g/l}$)			Mn ($\mu\text{g/l}$)		
			Range of concentrations detected*	Mean concentration	Range of concentrations detected	Mean concentration	Range of concentrations detected	Mean concentration	Range of concentrations detected	Mean concentration	
1	Hatton	8	<0.10	ND	<17.0	ND	<268.0	ND			
2	Watawala	8	0.1 – 9.9	1.2 \pm 3.1	<17.0	ND	<268.0	ND			
3	Ginigathena	8	5.3 – 16.5	8.8 \pm 3.4	<17.0	ND	<268.0	ND			
4	Nawalapitiya	8	5.0 – 8.6	6.9 \pm 0.9	<17.0	ND	<268.0	ND			
5	Ulapane	8	0.1 – 9.0	0.7 \pm 2.2	<17.0	ND	<268.0	ND			
6	Gampola	8	0.1 – 4.9	0.8 \pm 1.3	<17.0	ND	<268.0	ND			
7	Geliyoa	8	0.1 – 2.0	1.1 \pm 0.8	<17.0	ND	<268.0	ND			
8	Peradeniya	9	7.0 – 9.6	8.5 \pm 0.6	<17.0	ND	<268.0	ND			
9	Manampitiya	10	<0.1	ND	17.0 – 78.5	31.4 \pm 30.0	<268.0	ND			
10	Sungawila	8	0.1 – 4.4	0.5 \pm 1.2	17.0 – 112.5	27.7 \pm 26.3	<268.0	ND			
11	Somawathiya	8	0.1 – 6.0	1.9 \pm 3.8	17.0 – 87.9	27.5 \pm 19.6	<268.0	ND			
12	Mawilaru Anicut	8	0.1 – 14.2	1.7 \pm 3.9	17.0 – 26.4	18.2 \pm 3.0	<268.0	ND			
13	Seruniwara	8	0.1 – 671.3	78.9 \pm 171.1	17.0 – 51.3	28.3 \pm 10.1	268.0 – 1001.0	815.0 \pm 220.4			
14	Ralkuli Ferry	4	21003.1 – 28695.9	25012.0 \pm 3446.5	17.0 – 54.6	30.2 \pm 13.4	833.5 – 3619.1	1946.5 \pm 1176.0			
15	Upparu Ferry	4	13307.3 – 26343.7	19867.3 \pm 4991.5	17.0 – 41.4	28.1 \pm 8.3	533.0 – 2065.2	1313.4 \pm 727.0			
	Total	115									

ND – Less than relevant LOD; * Data presented as mean \pm standard deviation

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94 Table 3(continued). Range of concentrations detected and mean concentrations ($\mu\text{g/l}$) of heavy metals and metalloids detected in Mahaweli riverat different locations

No.	Location	No. of samples taken	Ni ($\mu\text{g/l}$)		Cu ($\mu\text{g/l}$)		As ($\mu\text{g/l}$)	
			Range of concentrations detected*	Mean concentration	Range of concentrations detected	Mean concentration	Range of concentrations detected	Mean concentration
1	Hatton	8	< 30.0	ND	0.1 – 2.6	0.6 ± 0.6	< 2.0	ND
2	Watawala	8	< 30.0	ND	0.1 – 1.9	0.5 ± 0.7	< 2.0	ND
3	Gimigathhena	8	< 30.0	ND	0.1 – 3.4	0.40 ± 0.8	< 2.0	ND
4	Nawalapitiya	8	< 30.0	ND	0.1 – 3.2	0.5 ± 1.0	< 2.0	ND
5	Ulapane	8	< 30.0	ND	0.1 – 4.5	0.5 ± 1.1	< 2.0	ND
6	Gampola	8	< 30.0	ND	0.1 – 18	2.8 ± 5.1	< 2.0	ND
7	Geliyoa	8	< 30.0	ND	0.1 – 1.2	0.3 ± 0.0	< 2.0	ND
8	Peradeniya	9	< 30.0	ND	0.3 – 4.6	1.1 ± 1.1	< 2.0	ND
9	Manampitiya	10	< 30.0	ND	0.1 – 39.9	2.1 ± 8.9	< 2.0	ND
10	Sungawila	8	< 30.0	ND	< 0.1	ND	< 2.0	ND
11	Somawathiya	8	30.0 – 50.0	31.3 ± 5.0	0.1 – 6.2	0.5 ± 1.5	< 2.0	ND
12	Mawilaru Anicut	8	30.0 – 55.5	31.6 ± 6.4	0.1 – 77.3	6.9 ± 19.6	2.0 – 2.2	2.0 ± 0.1
13	SeruNuwara	8	30.0 – 41.2	30.7 ± 2.8	0.1 – 4221.6	451.4 ± 1156.4	2.0 – 27.7	3.6 ± 6.4
14	Ralkuli Ferry	4	81.0 – 144.8	103.0 ± 21.9	8,324.9 – 10,953.1	$10,211.0 \pm 1,079.1$	202.2 – 270.5	233.5 ± 26.7
15	Upparu Ferry	4	30.0 – 85.7	48.8 ± 18.8	1,593.3 – 11,881.4	$8,251.9 \pm 3862.8$	238.6 – 366.9	298.6 ± 44.7
	Total	115						

ND – Less than relevant LOD; * Data presented as mean \pm standard deviation

Table 3(continued). Range of concentrations detected and mean concentrations ($\mu\text{g/l}$) of heavy metals and metalloids detected in Mahaweli riverat different locations

No.	Location	No. of samples taken	Se ($\mu\text{g/l}$)			Cd ($\mu\text{g/l}$)			Pb ($\mu\text{g/l}$)		
			Range of concentrations detected*	Mean concentration	Range of concentrations detected	Mean concentration	Range of concentrations detected	Mean concentration	Range of concentrations detected	Mean concentration	
1	Hatton	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
2	Watawala	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
3	Ginigathhena	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
4	Nawalapitiya	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
5	Ulapane	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
6	Gampola	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
7	Geliya	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
8	Peradeniya	9	< 38.0	ND	< 4.0	ND	< 186.0	ND			
9	Manampitiya	10	< 38.0	ND	< 4.0	ND	186.0–3,415.1	410.9 \pm 761.8			
10	Sungawila	8	< 38.0	ND	< 4.0	ND	186.0–343.2	197.6 \pm 39.5			
11	Somawathiya	8	< 38.0	ND	< 4.0	ND	< 186.0	ND			
12	Mawil-aruru Anicut	8	< 38.0	ND	4.0–4.8	4.1 \pm 0.2	186.0–267.7	191.1 \pm 20.4			
13	Serunuwara	8	38.5–315.4	72.2 \pm 75.1	4.0–5.4	4.1 \pm 0.4	< 186.0	ND			
14	Ralkuli Ferry	4	1,216.3–1571.0	1,361.1 \pm 144.3	< 4.0	ND	< 186.0	ND			
15	Upparu Ferry	4	1,146.1–1916.4	1,558.2 \pm 218.0	< 4.0	ND	< 186.0	ND			
	Total	115									

ND – Less than relevant LOD; * Data presented as mean \pm standard deviation

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96 Table 3(continued). Range of concentrations detected and mean concentrations ($\mu\text{g/l}$) of heavy metals and metalloids detected in Mahaweli riverat different locations

No.	Location	No. of samples taken	Hg ($\mu\text{g/l}$)		TI ($\mu\text{g/l}$)	
			Range of concentrations detected*	Mean concentration	Range of concentrations detected	Mean concentration
1	Haffton	8	< 4.0	ND	< 0.1	ND
2	Watawala	8	< 4.0	ND	< 0.1	ND
3	Ginigathhena	8	< 4.0	ND	< 0.1	ND
4	Nawalapitiya	8	< 4.0	ND	< 0.1	ND
5	Ulapane	8	< 4.0	ND	< 0.1	ND
6	Gampola	8	< 4.0	ND	< 0.1	ND
7	Geliyoa	8	< 4.0	ND	< 0.1	ND
8	Peradeniya	9	< 4.0	ND	< 0.1	ND
9	Manampitiya	10	< 4.0	ND	< 0.1	ND
10	Sungawila	8	< 4.0	ND	< 0.1	ND
11	Somawathiya	8	< 4.0	ND	< 0.1	ND
12	Mawil-arui Anicut	8	< 4.0	ND	< 0.1	ND
13	SeruNuwara	8	< 4.0	ND	< 0.1	ND
14	Ralkuli Ferry	4	< 4.0	ND	< 0.1	ND
15	Upparu Ferry	4	< 4.0	ND	< 0.1	ND
	Total	115				

ND –Less than relevant LOD; * Data presented as mean \pm standard deviation

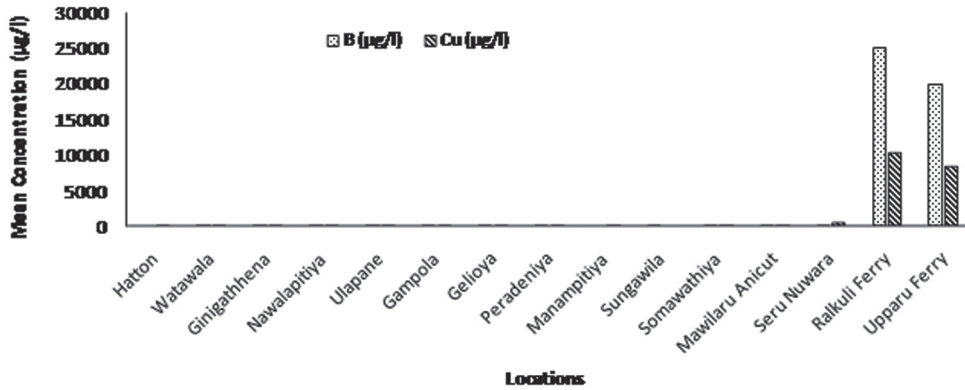


Figure 1. Mean concentration of Ba and Cu at each location

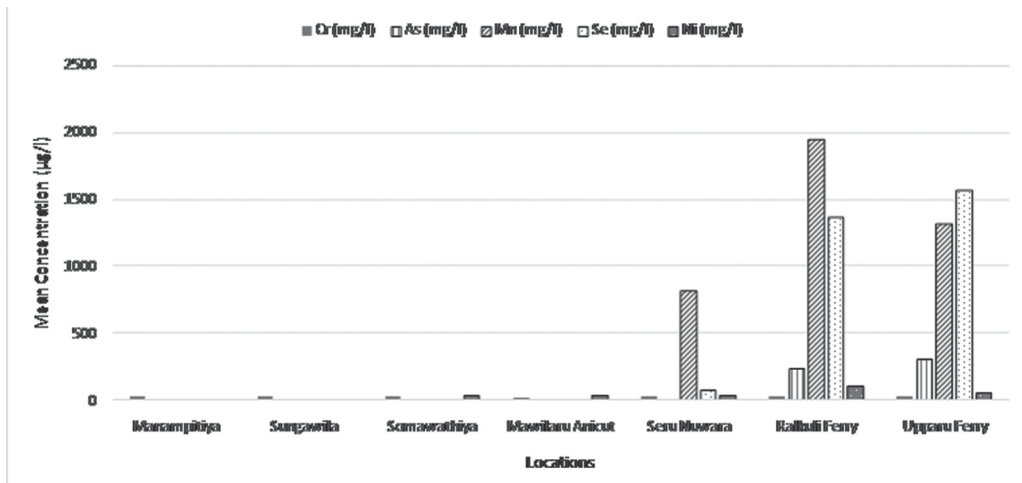


Figure 2. Mean concentrations of Cr, As, Mn, Se, and Ni at each location from Manampitiya to Upparu Ferry

The Cr and Ni concentrations in Mahaweli river water from Manampitiya to Upparu Ferry increased from 18.2–31.4 µg/land 30.0–103.0 µg/l, respectively. However, the mean concentrations of Cr were within the WHO permissible level (50.0 µg/l) though that of Ni in Rakkuli Ferry exceeded the WHO drinking water permissible level (70.0 µg/l). The mean concentrations of Se, Mn and As detected from Manampitiya to Upparu Ferry ranged from 72.2-1558.2 µg/l, 815.0-1946.5 µg/land 2.0-298.60 µg/l, respectively. The mean concentrations of Se and Mn detected in the water samples taken at Seru

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Nuwara, Ralkuli Ferry and Upparu Ferry exceeded the WHO permissible levels (40.0 µg/l and 400.0 µg/l, respectively), while As contents also exceeded its WHO permissible levels (10.0 µg/l) in the samples collected from Ralkuli Ferry and Upparu Ferry.

Cd and Pb

Low sensitivity of detection significantly hindered the comparison of contamination levels of Cd and Pb with the respective WHO permissible levels (3.00 µg/l and 10.00 µg/l, respectively). The LOD of these two elements were 4.0 µg/l for Cd and 186.0 µg/l for Pb. The data suggest that there may be chances of Pb levels being increased in future than the Cd levels in Mahaweli river water compared to the WHO permissible levels (Table 2).

The mean concentrations of Cd detected at Mavil-aru Anicut (4.0-4.80 µg/l) and Seru Nuwara (4.0-5.4 µg/l) were higher than the WHO permissible levels. Similarly, the mean concentrations of Pb detected at Manampitiya, Sungawila and Mawil-aru Anicut also exceeded the WHO permissible levels (Table 2).

In the midstream locations from Hatton to Peradeniya, only B and Cu were detected with the average concentrations between 0.4-2.8 µg/l. These concentrations were within the WHO permissible levels for potable water. However, as for the contamination levels of Cd and Pb, as discussed elsewhere, the Mahaweli river water from Hatton to Peradeniya could fall within the threshold values of health risks.

From Manampitiya to Mawil-aru Anicut the river was contaminated with Cu, B, Cr, Ni, As, Cd and Pb, out of the 11 elements analyzed. However, they did not exceed the WHO permissible levels (Table 2), except that of Cd (mean 4.1 µg/l) and Pb (mean 410.9 µg/l).

Manganese (Mn) was detected at the highest concentrations in Seru Nuwara followed by other elements with the concentration gradient of Mn>Cu>Pb>B>Se>Ni>Cr>Cd>As. The mean concentrations of Mn (78.9 µg/l), Se (72.2 µg/l), Cd (4.1 µg/l) and Pb (<186.0 µg/l) exceeded the respective WHO permissible levels (Table 2). The higher levels of above elements could be attributed to the presence of industrial, agricultural discharges and direct sewage discharges along the Mahaweli river.

River water collected at locations from Rulkuli Ferry to Upparu Ferry indicated that B was present at the highest mean concentration in both locations with the concentration gradient of B>Cu>Mn>Se>As>Pb>Ni>Cr>Cd for Rukuli Ferry, and B>Cu>Se>Mn>As>Pb>Ni>Cd>Cr for *Upparu Ferry*. The mean concentrations of the elements reported at the two locations of Rukuli Ferry and Upparu Ferry were Se (1,361.1 and 1,558.2 µg/l, respectively), Ni (103.0 and 48.8 µg/l), Cu (10,211.0 and 8,251.9 µg/l, respectively), As (233.5 and 298.6 µg/l, respectively), B (25,012.0; 19,867.3µg/l, respectively), Cr (30.2 and 28.1 µg/l) and Mn (1,946.5 and 1,313.4 µg/l, respectively). Except for Cr, all the other mean concentrations of the above elements exceeded the WHO permissible levels (Table 2). Thallium and Hg concentrations were less than the LODs. These heavy metal contaminations could be due to the influx of sea water into the river water.

The highest mean concentration of B, Mn, Ni and Cu were reported from Rulkali Ferry while As and Se were reported in Upparu Ferry. The highest mean concentration of Cr and Pb were reported from Manampitiya and water taken from Mawil-arū Anicut and Seru Nuwara reported the highest mean concentration of Cd.

CONCLUSIONS

The results of the present study confirmed that contamination of Hg and Tl in Mahaweli river is negligible while the river water from upstream locations at Hatton to Peradeniya is not highly contaminated with the elements As, B, Cr, Cu, Mn, Ni, and Se. In contrast, Mahaweli river water at Manampitiya, Seru Nuwara, Ralkuli Ferry and Upparu Ferry was highly contaminated with some of the heavy metals, and thus, requires purification systems to remove such metals prior to being used for drinking or cooking purposes.

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