



www.cafetinnova.org

Indexed in  
Scopus Compendex and Geobase Elsevier, Chemical  
Abstract Services-USA, Geo-Ref Information Services-USA,  
List B of Scientific Journals, Poland,  
Directory of Research Journals

**International Journal  
of Earth Sciences  
and Engineering**

April 2015, P.P.343-353

ISSN 0974-5904, Volume 08, No. 02

## Variation of Trace Metals in Liquid and Suspended Phases of Water in Middle and Lower Catchments of River Mahaweli, Sri Lanka

A G P ARAVINNA<sup>1,2</sup>, N PRIYANTHA<sup>2</sup>, H M T G A PITAWALA<sup>2,3</sup> AND S K YATIGAMMANA<sup>2,4</sup>

<sup>1</sup>Chemical and Environmental Section, Central Engineering Consultancy Bureau, Colombo, Sri Lanka

<sup>2</sup>Postgraduate Institute of Science, <sup>3</sup>Department of Geology, <sup>4</sup>Department of Zoology, University of Peradeniya, Peradeniya, Sri Lanka

Email: piyalaravinna@yahoo.com

**Abstract:** Variation of trace metals in phases of liquid and suspended solid of surface water bodies of lower and middle catchments of Mahaweli river basin was assessed to understand the contribution of suspended solids for the transportation of trace metals within the basin. Contents of dissolved and acid extractable metals (Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn) were determined against the load of suspended solids in dry and rainy seasons. Levels of Cd and Pb in liquid and suspended phases are below the minimum detection level with a few exceptions. Correlation analysis indicates that there is a significant difference in trace metal levels between the liquid and suspended phases. Correlation among the weight of suspended solids and trace metals carried by them is very poor for Cu, Cr, Ni and Zn ( $R^2 < 0.2$ ). Variation of trace metal levels among different types of surface water bodies studied is insignificant except agricultural canals. Results of the study revealed that anthropogenic activities do not affect much on middle and lower catchment of River Mahaweli in terms of trace metals.

**Keywords:** Water Quality, Suspended Solids, Heavy Metals, Mahaweli River Basin, Irrigation Canals

### 1. Introduction

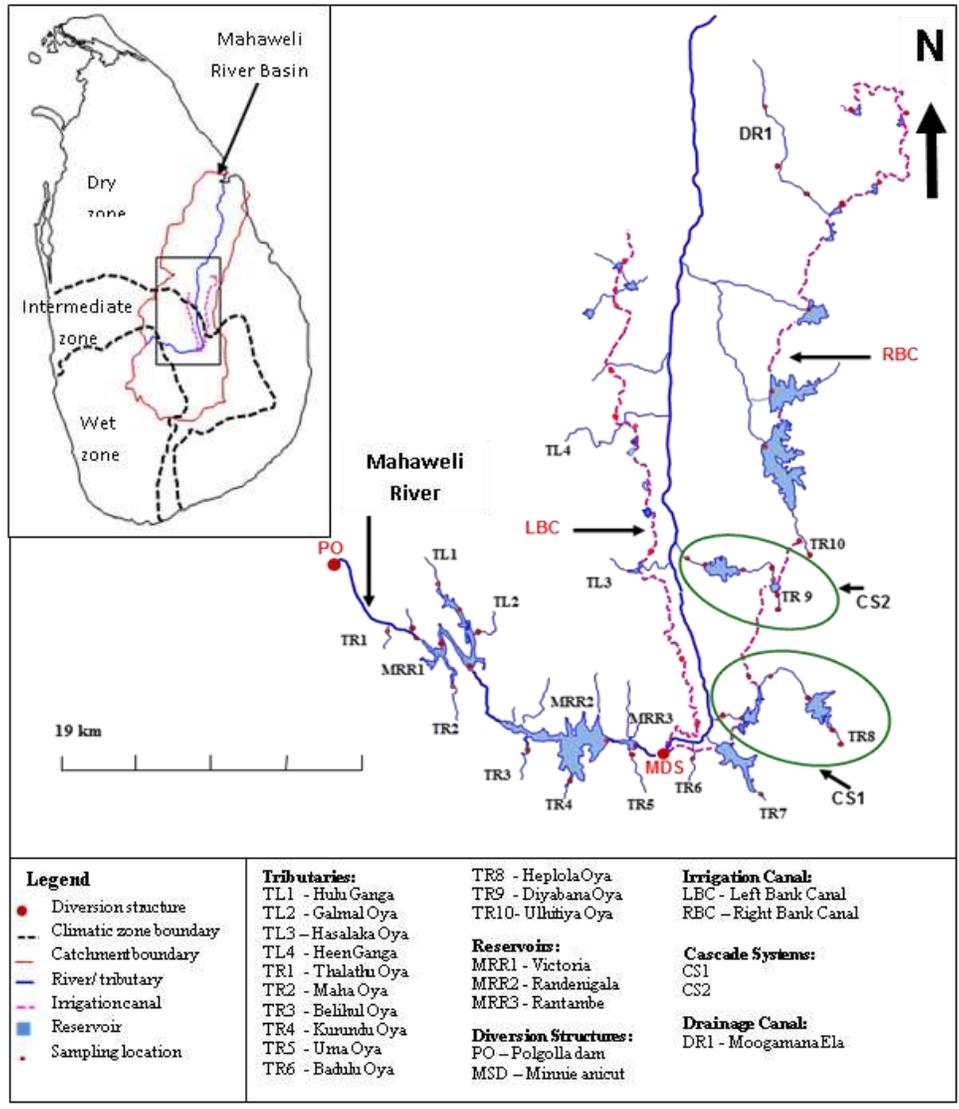
Heavy metals of anthropogenic or natural origin are released to soil, water and air [1]-[3]. Environmental pollution by trace metals is a major issue in many developing countries, including Sri Lanka [4]-[6]. Industrialization, urbanization and poor catchment management could enhance the above situation. 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 biochemical processes of plants and animals. However, at high concentrations, these trace metals become toxic [7]. Mahaweli River (MR), the longest river and Mahaweli river basin (MRB) is the largest river basin (10,300 km<sup>2</sup>) in Sri Lanka. The total area of Upper Catchment of Mahaweli River (UCMR) is 5680 km<sup>2</sup> (above the elevation of 150 m), and 25% of the area has been utilized for tea plantation and vegetable cultivation [8]. Fifteen percent of the human population of Sri Lanka is found in MRB [9]. Levels of Cr, Mn, Co, Cu, Fe and Zn in surface soils of agricultural lands of UCMR are higher than those in natural soils in the area [10].

Water of UCMR has been diverted by the Accelerated Mahaweli Development Project (AMDP) to provide irrigation water for dry and intermediate zones of the country [11] (Figure 1). The mean annual rainfall varies from 1650 mm to 5300 mm in UCMR [12]. Since MR

receives considerable fraction of total discharge from agricultural lands and urban areas, there is a potential risk to distribute trace metals from upper catchment to its lower catchment. Victoria (MRR1), Randenigala (MRR2) and Rantambe (MRR3) are three major storage reservoirs of MR, and water from these reservoirs is distributed to paddy lands of the banks of MR through left bank canal (LBC, 74 km long) and right bank canal (RBC, 85 km long) (Figure 1). Many researchers speculate that heavy metals, such as Cd and As, in water and food would be a possible cause for the prevalence of chronic kidney disease of unknown aetiology (CKDu) in the North Central Province (NCP) and other regions of Sri Lanka [13]-[17].

Some heavy metals moved in water as hydrated ions or soluble forms of organic and inorganic complexes [1], while some heavy metals are easily adsorbed on soil particles, insoluble phase of metal oxides, and suspended organic matters.

This adsorption occurs through the relatively weak physical bonds or strong chemical bonds [18]-[19]. Suspended particles which are contaminated by heavy metals may transfer to water bodies and deposit in the reservoirs bottoms with sediments. Both aqueous and suspended phases would play crucial role for the transportation of heavy metals from catchment to water bodies.



**Figure 1:** Map of the study area of Mahaweli river basin in Sri Lanka showing MR, its tributaries, reservoirs associated with MR, diversion structures, irrigation canals, reservoirs of LB and RB, and sampling locations. Insert: Map of Sri Lanka showing location of Mahaweli river basin and distribution of major climatic zones in the country.

Even though levels of trace metals have been reported in surface water of adjacent river basins (Maduru Oya basin and Kala Oya basin), which receives diverted water from MR, [20]-[21] the studies are very limited for middle and lower catchment of MR. Further, comprehensive study has not been conducted to understand the contribution of suspended solids for the transportation of trace metals in water bodies which are specially constructed for the irrigation.

## 2. Methodology

### 2.1. Study Area

Major fraction of the study area is located in the Central and Uva Provinces of Sri Lanka. Thirteen tributaries,

including four major tributaries (TL1, TL2, TR5 and TR10), irrigation canals (LBC and RBC) originated from the Minipe diversion structure (MSD), main storage reservoirs of MR (MRR1, MRR2 and MRR3), two major cascade irrigation systems (CS1 and CS2) of LB and RB, and one major drainage canal (DR1) were selected for the study (Figure 1). Sampling locations demarcated for thirteen tributaries (single representative location of each tributary), LBC, RBC, CS1, CS2, DR1 and MR, and numbers of locations selected for sampling from each water bodies are 13, 13, 14, 6, 7, 3 and 10, respectively (Figure 1).

### 2.2. Selected Parameters for the Study

Onsite measurements of pH and electrical conductivity (EC) were taken with the help of portable pH meter (Hanna HI98101) and conductivity meter (Hanna HI98303) with standard calibrations. Representative surface water samples were collected at the depth of 0.3 - 0.6 m (from the surface of water body) in plastic containers using a plastic grab sampler. Samples were filtered through pre cleaned 0.45  $\mu\text{m}$  membrane filter and acidified with conc.  $\text{HNO}_3$  (VWR, UK) to  $\text{pH} < 2$  and sorted at 4  $^\circ\text{C}$  to determine dissolved metal contents of Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn. The same procedure was followed without filtration to determine the acid extractable metal content of samples. Dissolved oxygen of samples was fixed by Winkler reagent. Preserved samples were transported to the Analytical Research Laboratory of the Department of Chemistry, University of Peradeniya, Sri Lanka for analysis of heavy metals. Total dissolved solid (TDS) and total suspended solid (TSS) of each sample were determined by gravimetry using larger volumes (0.5 L to 1.0 L) [22]. The minimum detection limit (MDL) for both of TDS and TSS is 1.0  $\text{mg L}^{-1}$ . Water samples (500 mL) were extracted with conc.  $\text{HNO}_3$  (5 mL per 100 mL sample) to determine acid extractable metal content of the samples. Acid extractable and dissolved metal levels of Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn in samples were determined using *Thermo M series* graphite furnace atomic absorption spectrophotometer (GFAAS) and selected wavelengths for the analysis of Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn are 309.3, 228.8, 324.8, 357.9, 248.3, 279.5, 232.0, 217.0 and 213.9 in nm, respectively. Loss on ignition of TSS of samples ( $\text{LOI}_{\text{TSS}}$ ) was determined to estimate content of suspended organic matter. Mass of insoluble content of acid extracts ( $\text{TSS}_{\text{INS}}$ ) was determined to estimate acid insoluble matters. All laboratory analysis and quality controlling steps were done in accordance with standard methods. The minimum detection limits of Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn are 4.0, 0.6, 1.8, 1.3, 5, 0.4, 2.2, 2.0 and 0.3 in  $\mu\text{g L}^{-1}$ , respectively. Content of heavy metals in suspended particles ( $M_{\text{TSS}}$ , particle size  $> 0.45 \mu\text{m}$ ) was calculated using Equation 1.

$$M_{\text{TSS}} = M_{\text{AE}} - M_{\text{D}} \quad (1)$$

Where,  $M_{\text{D}}$  and  $M_{\text{AE}}$  are content of acid extractable heavy metal and content of dissolved heavy metal in the samples, respectively.

Mass percentage of acid extractable metals considered in the study ( $T_{\text{AE(TSS)}}\%$ ) were estimated using Equation (2) to the estimate availability of other soluble inorganic minerals.

$$T_{\text{AE(TSS)}}\% = \frac{(\sum M_{\text{AE}})}{\text{TSS}} \times 100\% \quad (2)$$

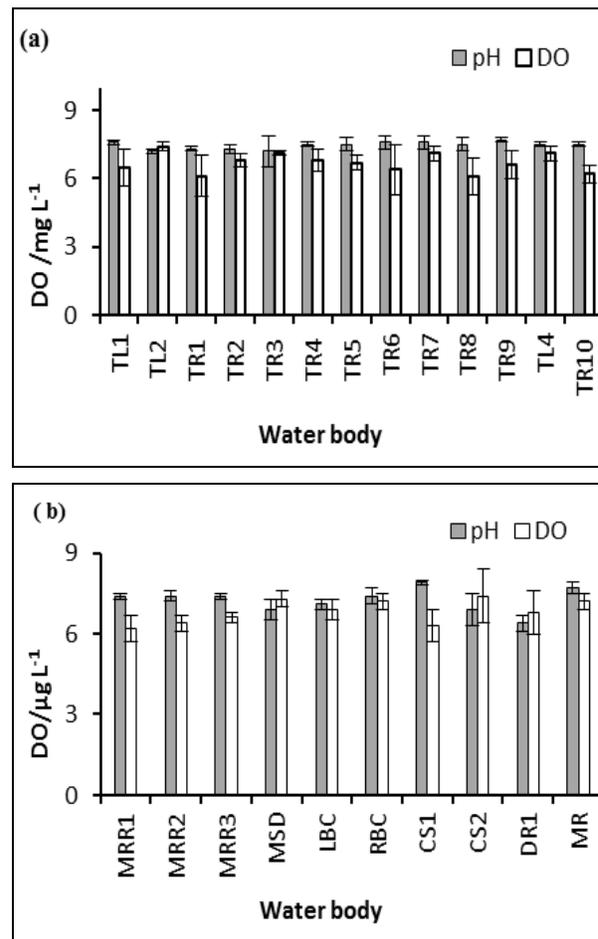
### 2.3. Monitoring Period

Water sampling was carried out during dry period (August 2012) and rainy period (in December 2013 and in March 2014) for three times per season.

## 3. Results and Discussion

### 3.1. Basic Physio-Chemical Properties

Water temperature of the study sites was within the range of 19 – 34  $^\circ\text{C}$ . However, no variation of pH was detected among the water bodies during the monitoring period (Figure 2). Levels of TSS in cascade reservoir of MR are significantly lower than those of the moving water in irrigation and drainage canals (LBC, RBC and DR1) and tributaries (Figure 3), and TSS levels in tributaries are significantly higher in rainy periods than those on dry occasions showing relatively high erosion rates. Electrical conductivity (EC) and TDS (138 - 220  $\text{mg L}^{-1}$ ) of DR1 is significantly higher than that of other water bodies showing relatively high levels of dissolved solids (Figure 4).



**Figure 2:** Variations of pH, and DO in; (a) tributaries of MR; (b) cascade reservoirs of MR, cascade irrigation systems of RB, major irrigation canals of MR, and MR downstream of MSD

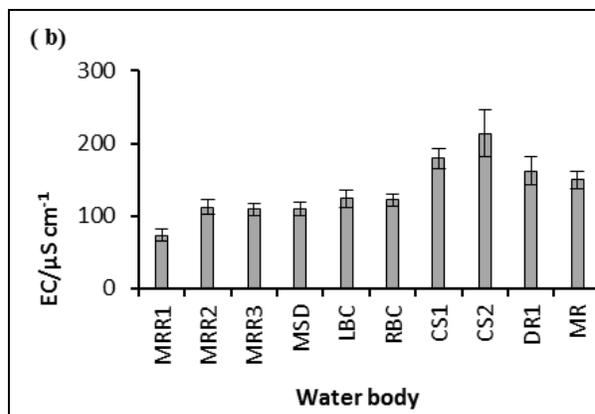
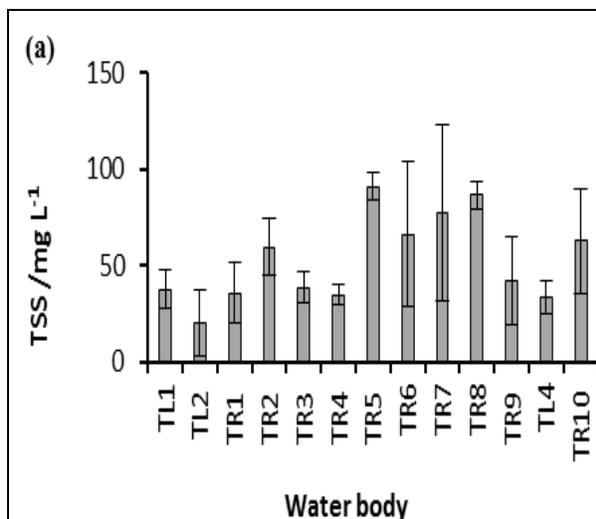


Figure 4: Variations of EC in; (a) tributaries of MR; (b) cascade reservoirs of MR, cascade irrigation systems of RB, major irrigation canals of MR, and MR downstream of MSD

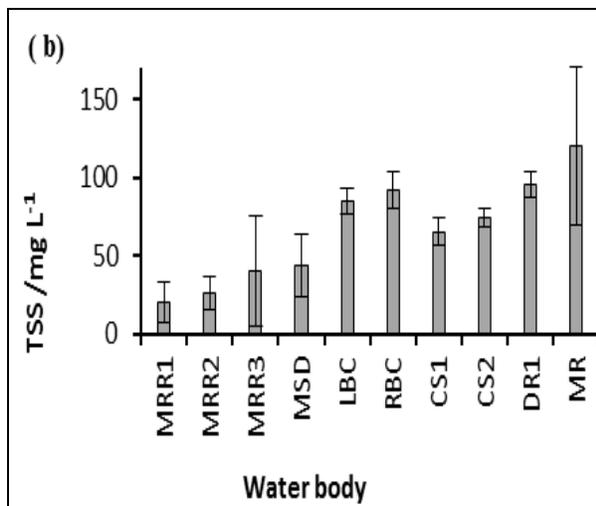
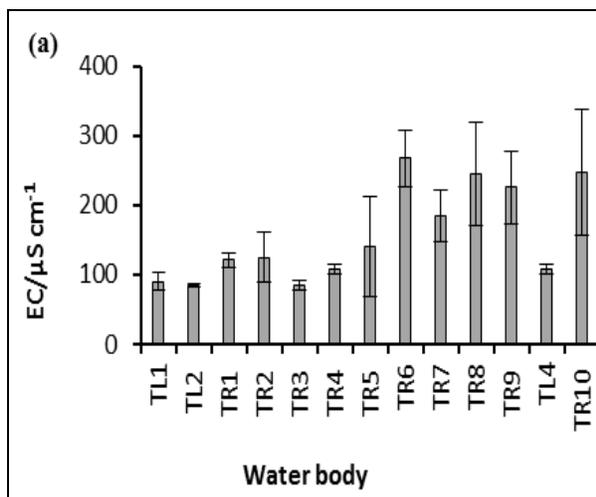


Figure 3: Variations of TSS in; (a) tributaries of MR; (b) cascade reservoirs of MR, cascade irrigation systems of RB, major irrigation canals of MR, and MR downstream of MSD.



### 3.2. Distribution of Fe, Al and Mn in water bodies

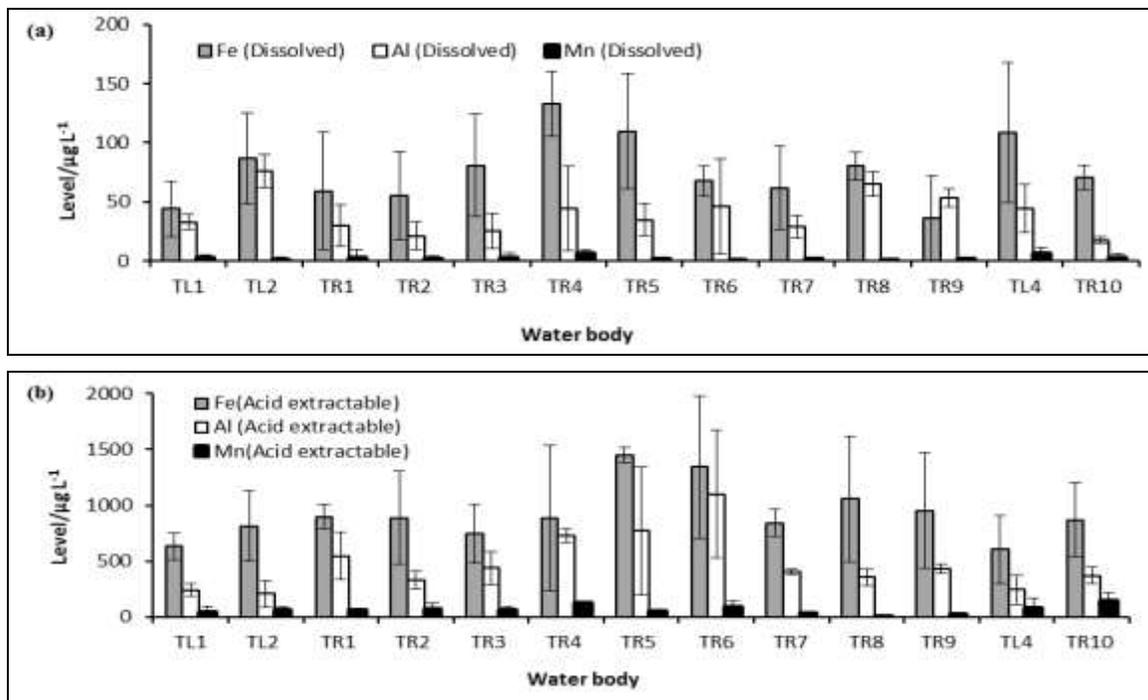
Iron (Fe), Al and Mn are three major trace metals detected in water bodies of the study region. The sequence of Fe, Al, Mn in soluble forms and acid extractable forms in all water bodies of MRB in both seasons is Fe < Al < Mn (except CS1, CS2 and DR1). Abundance of Al and Fe in earth's crust are about 8% and 5%, respectively [23]-[24] proving the high abundance. Levels of dissolved Al ( $Al_D$ ) and acid extractable Al ( $Al_{AE}$ ) in the water bodies studied are (6.4 - 89.6)  $\mu\text{g L}^{-1}$  and (24.8 - 1051.5)  $\mu\text{g L}^{-1}$ , respectively. Aluminium occurs naturally in the environment as silicates, oxides and hydroxides, combined. The major clay mineral of the soils of the study area is kaolinite (40% - 60%) [25]. Acidic environments or acid rain on aluminium rich mineral can cause an increase in the dissolved aluminium content of the surrounding waters [26]-[27]. Aluminium can exist as hydroxides, fluorides, sulfates, phosphates, bicarbonates, and silicates within the aqueous environment [28]. Stability and solubility of Al is increased when the pH of aqueous solution is decreased. Levels of pH of all water bodies studied are close to neutral condition (7.1 - 8.1). Presence of fluoride is also increases the solubility of Al, forming a complex ion. However, fluoride levels of surface water are also very low [29]. Literature shows that Al levels in water vary in the range of 1 - 50  $\mu\text{g L}^{-1}$  near neutral pH [27] proving the results. Levels of  $Al_D$  in DR1 and the cascade irrigation systems (CS1 and CS2) are significantly higher than those in other water bodies without much variation of DO and pH (Figure 5a) showing the complexness of the aluminium chemistry. Further, levels of  $Al_D$  are always significantly lower than the  $Al_{AE}$  level of the water bodies studied (Figure 5 and 6). However, the concentration of Al in natural waters can vary significantly depending on various physicochemical and mineralogical factors [27]-[28].

Clay mineral such as aluminium silicates and aluminium salt precipitated in suspended solids would be responsible for high  $Al_{AE}$  in the water bodies.

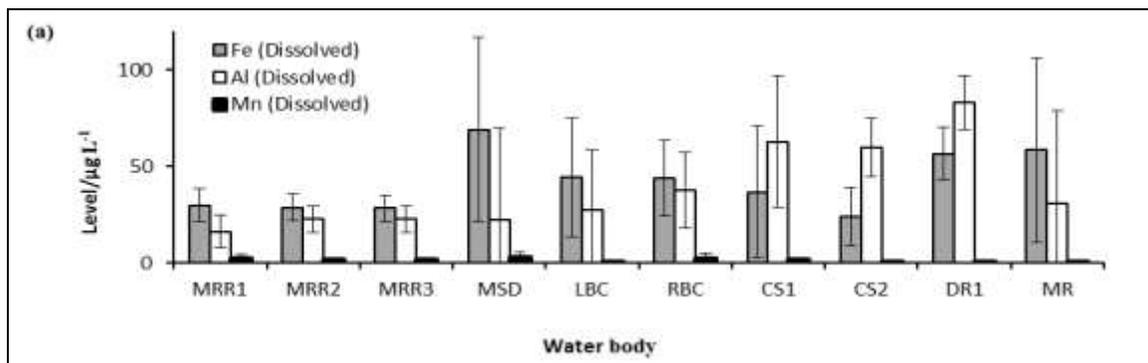
The levels of dissolved iron ( $Fe_D$ ) and levels of acid extractable Fe ( $Fe_{AE}$ ) in the water bodies studied are in the ranges of (0.7 - 176.2)  $\mu\text{g L}^{-1}$  and (64.0 - 2450.0)  $\mu\text{g L}^{-1}$ , respectively. The main soil types of the catchment of MR are red-yellow podzolic and reddish brown earth. Hematite and goethite (rich with iron) are major two minerals in soils [25], [30]-[31]. Therefore, it is proven that the movement of high levels of Fe is found in water bodies. Aqueous Fe(III) and Fe(II) are stable in natural water only in the absence of dissolved oxygen [32]. When oxic condition is dominated, Fe(II) is converted to the Fe(III) forming insoluble oxides of  $\text{Fe}_2\text{O}_3$ . All water samples studied were collected within 30 - 60 cm depth from the surface (DO level: 6.9 - 9.1 mg/L).

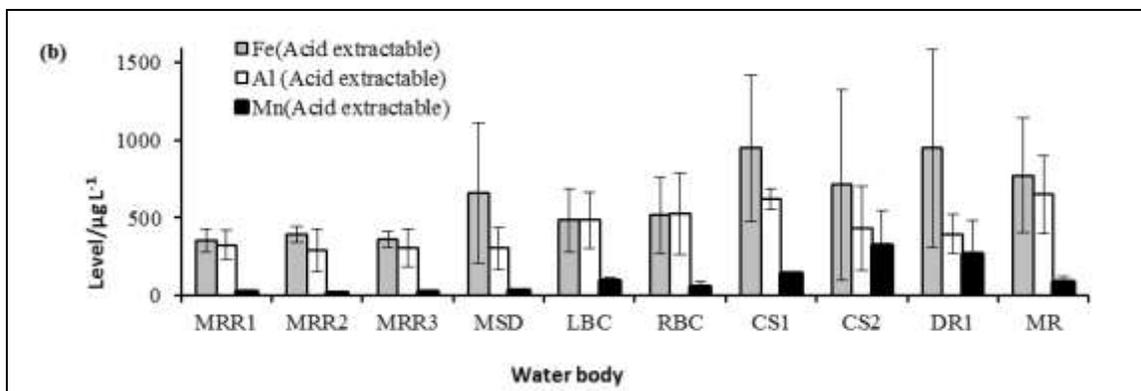
Hence, this oxic environment facilitates for high conversion rate of soluble Fe ions to insoluble form of  $\text{Fe}_2\text{O}_3$ . Therefore, the gaps between  $Fe_D$  and  $Fe_{TE}$  is very high (Figure 5 and 6).

The levels of dissolved manganese ( $Mn_D$ ) and levels of acid extractable manganese ( $Mn_{AE}$ ) in the water bodies studied are in the ranges of (0.2 - 20.4)  $\mu\text{g L}^{-1}$  and (9.1 - 324.1)  $\mu\text{g L}^{-1}$ , respectively. Manganese can exist in many oxidation states and the most common oxidation states of Mn of environmentally and biologically important compounds are  $\text{Mn}^{2+}$ ,  $\text{Mn}^{4+}$  or  $\text{Mn}^{7+}$  [33]. Manganese also behave as iron, and stability of insoluble oxides of Mn(III/VI) is higher than that of aqueous species of Mn(II)[32]. Due to oxic condition of the water studied, the gaps between  $Mn_{AE}$  and  $Mn_D$  for all water bodies are very high (Figure 5 and 6).



**Figure 5:** Variations of (a) dissolved forms of Fe, Al and Mn (b) acid extractable Fe, Al and Mn in tributaries of middle and lower catchment of MR





**Figure 6:** Variations of (a) dissolved forms of Fe, Al and Mn (b) acid extractable Fe, Al and Mn in cascade reservoirs of MR, cascade irrigation systems of RB, major irrigation canals of MR, and MR downstream of MSD

### 3.3. Distribution of Lesser Abundance Traces Metal in Water Bodies

Level of dissolved Cd in all water bodies studied are below the MDL ( $0.6 \mu\text{g L}^{-1}$ ) and acid extractable Cd was detected only in one sample ( $1.3 \mu\text{g L}^{-1}$ ) out of 143 samples. Cd available in soil solution is rapidly adsorbed to the clay mineral [34]. However, desorption

ability of Cd from the soil is very low at neutral the pH condition [35]. Even though some literature [36] have reported relatively high Cd in some tributaries of the study area, the results of this study show that acid extractable Cd levels are below  $0.6 \mu\text{g L}^{-1}$  in same tributaries except one location of MR.

**Table 1:** Detection profile of lesser abundant trace metals (total number of sample analyzed is 143)

Metal	MDL / $\mu\text{g L}^{-1}$	Content of metal / $\mu\text{g L}^{-1}$		Number of sample above MDL
		Mean	Range	
$Cd_D$	0.6	BMDL	BMDL	0
$Cd_{AE}$	0.6	1.3	BMDL - 1.3	1
$Cu_D$	1.8	$3.5 \pm 2.0$	BMDL - 9.3	73
$Cu_{AE}$	1.8	$5.2 \pm 4.2$	BMDL - 31.7	80
$Zn_D$	0.3	$5.2 \pm 4.8$	BMDL - 32	83
$Zn_{AE}$	0.3	$6.3 \pm 4.8$	BMDL - 25	98
$Cr_D$	1.3	$1.0 \pm 1.1$	BMDL - 5.1	84
$Cr_{AE}$	1.3	$18.0 \pm 5.9$	BMDL - 38.9	92
$Ni_D$	2.2	$4.2 \pm 4.0$	BMDL - 19.5	72
$Ni_{AE}$	2.2	$6.1 \pm 4.4$	BMDL - 23	79
$Pb_D$	2.0	BMDL	BMDL- 2.2	1
$Pb_{AE}$	2.0	2.5	BMDL- 2.8	2

BMDL – below minimum detection limits.

Fertilizer and agrochemicals are major sources of the Cd. Relatively high Cd levels have been reported in long running agricultural land in UCMR [10]. Even though soil collides contaminated with Cd would be transported to the water bodies through tributaries by erosion, high precipitation rates of UCMR [12] cause dilution of contaminated soil collides (range of average TSS levels:  $20.1 - 101.3 \text{ mg L}^{-1}$ ). This would be the probable reason for the low total cadmium levels in the tributaries. Levels of dissolved Pb in all water bodies are below MDL ( $2.2 \mu\text{g L}^{-1}$ ). Acid extractable Pb levels also below MDL, except two locations (LBC and CS1) and it corresponds to 1% of the total samples. However,

this indicates low levels of industrial pollution in the catchment.

Levels of dissolved and acid extractable Zn, Cr, Ni and Cu were detected below  $40 \mu\text{g L}^{-1}$ . There are significant differences among dissolved and acid extractable metal levels of Zn, Cr, Ni and Cu.

Significant deference was observed among levels of dissolved zinc ( $Zn_D$ ) and acid extractable zinc ( $Zn_{AE}$ ), and their ranges are (BMDL -  $9.0 \mu\text{g L}^{-1}$ ) and (BMDL -  $17.4 \mu\text{g L}^{-1}$ ), respectively. Zinc occurs in small amounts in almost all igneous rocks. The natural zinc content of some soils is estimated to be  $1-300 \text{ mg kg}^{-1}$  [37]. Zinc content of surface horizons of agricultural soils from

low country and up country of Sri Lanka is  $227 \pm 106 \text{ mg kg}^{-1}$  [10]. Further,  $\text{Zn}^{2+}$  is readily adsorbed on clay mineral [38]. Zinc adsorbed on clay minerals and naturally available Zn in acid soluble minerals is responsible for the situation.

Levels of dissolved copper ( $Cu_D$ ) vary from BMDL to  $18.1 \mu\text{g L}^{-1}$  while the levels of acid extractable copper ( $Cu_{TE}$ ) vary from BMDL to  $31.7 \mu\text{g L}^{-1}$ . Even though there is difference between the  $Cu_D$  and  $Cu_{TE}$ , difference is smaller than those for Zn. The fate of elemental copper in water is complex and influenced by pH, dissolved oxygen and oxidizing agents and chelating compounds or ions [39]. Cu(II) is the major stable species in water up to pH 6. Aqueous  $\text{CuCO}_3$  is prevalent at pH 6 – 9 [40]. Aqueous copper strongly adsorbs to clay minerals in a pH dependent fashion, and adsorption is increased by the presence of particulate organic materials [41]-[42]. However, naturally available copper compound in soil and copper compounds coming from industries and agrochemicals (fertilizer and fungicides) would be a probable reason for the above detected levels.

Maximum detected dissolved and acid extractable Ni levels ( $Ni_D$  and  $Ni_{AE}$ ) are  $19.5 \mu\text{g L}^{-1}$  and  $25.7 \mu\text{g L}^{-1}$ , respectively. Ni occurs naturally in the earth's crust with an average concentration of 0.008 percent. Nickel occurs predominantly as the ion  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  in natural waters at pH 5–9 [43]. The nickel concentration of fresh surface water has been reported to average between 15 and  $20 \mu\text{g L}^{-1}$  in the world [44].

In natural environments, the most stable oxidation states of chromium are Cr(III) and Cr(VI). Cr(III) is not significantly migrated in natural systems because readily precipitate in neutral to alkaline pH range [45]. Therefore, dissolved Cr ( $Cr_D$ ) level is varies from BMDL to  $5.1 \mu\text{g L}^{-1}$  and range of acid extractable Cr ( $Cr_{AE}$ ) remain within the range of 3.9 –  $17.1 \mu\text{g L}^{-1}$ . The distribution of compounds containing Cr(III) and Cr(VI) depends on the redox potential, the pH and the presence of oxidizing or reducing compounds in aqueous medium [46]. There is slight difference among the levels of  $Cr_D$  and  $Cr_{AE}$ . In soil, Cr(III) is predominates and Cr(VI) can easily be reduced to Cr(III) by organic matter [46]. Most surface water contains Cr in the range of 1 -  $10 \mu\text{g L}^{-1}$ . However, suspended clay particles are able to adsorb Cr(III) at about  $0.5 \text{ mmol g}^{-1}$  [47]-[48] and this would be the reason for the relatively high  $Cr_{AE}$  than  $Cr_D$ .

### 3.4. Variation of trace metal among the water bodies

Levels of  $Mn_{TE}$  and  $Fe_{AE}$  were significantly higher in moving surface water (of tributaries) than in those in stagnated surface water in MRR1, MRR2 and MRR3 (Figure 5 and 6). Total suspended solid levels are also

behaved in similar manner (Figure 3). Settlement of TSS including oxides of Mn (III/VI) and Fe(III) is responsible for relatively low level of  $Mn_{AE}$  and  $Fe_{AE}$  in those water bodies.

Variation levels of  $Mn_{AE}$  in cascade irrigation systems (CS1 and CS2) and drainage canal (DR1) is relatively high, while the levels of  $Mn_D$ , DO and pH remain stable (Figure 6a and 6b).

Further, levels of  $Al_D$  in CS1, CS2 and DR1 higher than that of other reservoirs. Levels of EC of DR1, CS1 and CS2 were relatively higher than those of other water bodies and it is the only difference observed in the period of study. Unfortunately justifiable evidences are not available in literature to explain the situation and further studies are required to explain the situation.

Levels of  $Fe_{AE}$ ,  $Al_{AE}$  and  $Mn_{AE}$  of MR (downstream of MDS) are significantly higher in rainy season than those in dry season. TSS level also behaves similarly in MR. Unsettled clay minerals and oxides of Mn(III/VI), Fe(III) and Al(III) in TSS may be responsible for the situation.

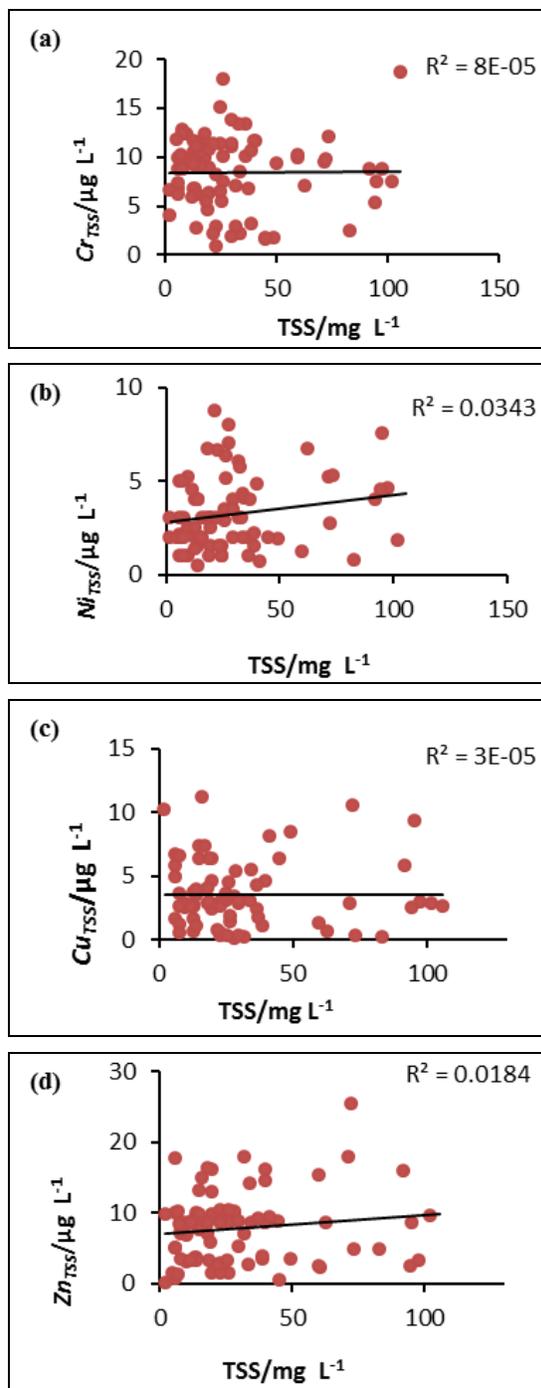
### 3.5. Suspended solid and movement of trace metal

Percentage loss on ignition is smaller 10 % of TSS (for samples having TSS greater than  $10 \text{ mg L}^{-1}$ ). Therefore, clay minerals and other precipitated salts are responsible for the TSS of the majority of the samples analysed. Levels of  $M_{TSS}$  ( $Cr_{TSS}$ ,  $Ni_{TSS}$ ,  $Cu_{TSS}$  and  $Zn_{TSS}$ ) were plotted against TSS for the samples having  $LOI_{TSS} < 10\%$  (content of inorganic mass in TSS > 90%). However, relationship among TSS and  $M_{TSS}$  is very poor for Cr, Ni, Zn and Cu ( $R^2 < 0.1$ , Figure 7).

Percentage of  $TSS_{INS}$  varies within the range of 65 - 92 % (for the samples having TSS >  $10 \text{ mg L}^{-1}$ ) while  $T_{AE(TSS)}$  varying within the range of 0.1 – 8.5%. Difference between  $TSS_{INS}$  % and  $T_{AE(TSS)}$  % shows availability of other acid soluble compound.

Therefore, considerable quantity of other acid soluble compounds is available with TSS. Literature shows that levels of Mg and Ca in the study area are reported within  $20 \text{ mg L}^{-1}$  and  $40 \text{ mg L}^{-1}$ , respectively [49]. Therefore, Ca and Mg compounds precipitated with TSS would act as acid soluble compounds.

However, in addition to the elements adsorbed on clay minerals, significant fraction of acid soluble precipitates and minerals are present with TSS in the study region.



**Figure 7:** Correlation between TSS and insoluble fraction of trace metals of (a) Cr, (b) Ni, (c) Cu and (d) Zn in water sample studied.

### 3.6. Contribution of acid extractable Fe and Al compound for the transportation of traces metal

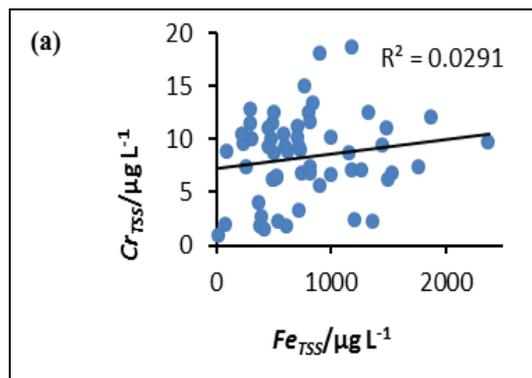
Oxides of Al, Fe and Mn play an important role for the sorption of heavy metals [50]. Adsorption studies show that manganese oxides and iron oxides adsorb heavy metals strongly.

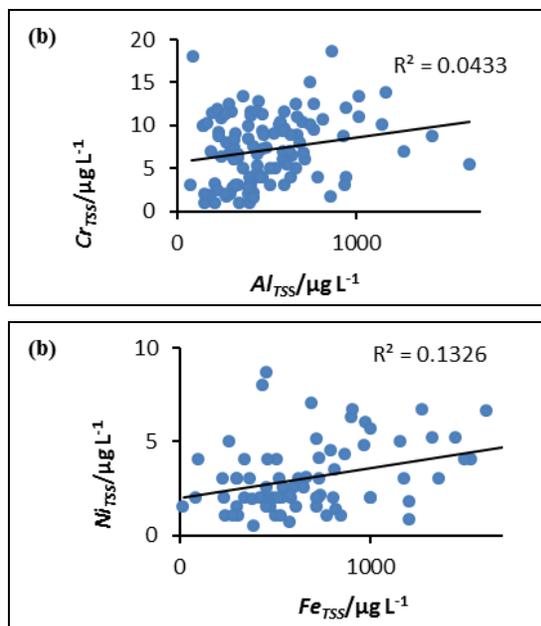
Correlations among  $M_{TSS}$  of higher abundance metal ( $Fe_{TSS}$ , and  $Al_{TSS}$ ) and  $M_{TSS}$  of trace metals ( $Cr_{TSS}$ ,  $Ni_{TSS}$ ,  $Cu_{TSS}$  and  $Zn_{TSS}$ ) are very poor ( $R^2 < 0.13$ ). However, correlations between (i)  $Fe_{TSS}$  and  $Cu_{TSS}$ ; (ii)  $Al_{TSS}$  and  $Cu_{TSS}$ ; (iii)  $Al_{TSS}$  and  $Ni_{TSS}$ ; (iv)  $Al_{TSS}$  and  $Zn_{TSS}$ , are very poor compared to the correlations amongst of (i)  $Fe_{TSS}$  and  $Cr_{TSS}$ ; (ii)  $Fe_{TSS}$  and  $Ni_{TSS}$ ; (iii)  $Fe_{TSS}$  and  $Zn_{TSS}$ ; (iv)  $Al_{TSS}$  and  $Cr_{TSS}$ .

Adsorption of  $Ni^{2+}$  and  $Cr^{3+}$  is believed to occur on iron oxide. This adsorption increases with increase in pH or alkalinity [51].

Very low correlation between  $Fe_{TSS}$  and  $Cu_{TSS}$ , can be attributed to neutral pH conditions.  $Cu^{2+}$  adsorbed to alumina surface forming Cu-O-Al bond by chemisorption. This adsorption is increased within the pH range of 4.5 - 6.0. However, fraction of  $Cu^{2+}$  adsorbed on clay or alumina is precipitated as  $Cu(OH)_2$  which is readily re-dissolved. The nature of Cu adsorbed [Cu-O-Al or  $Cu(OH)_2$ ] may vary with the type of clay mineral (boehmite, gibbsite, alumina) [52] which are available in aqueous phase. This would be the probable reason for very low correlation among the  $Al_{TSS}$  and  $Cu_{TSS}$ .

Fe(II) in aqueous solution involved in Cr(VI) reduction [53]-[55]. However, due to oxic environment of the studied water, stability of Fe(II) is minimum. Mn(IV) is also responsible for the oxidation of Cr species to Cr(VI) [53]-[55]. Cr(VI) formed by Mn(IV) in aqueous medium readily adsorbed by iron oxides. Even though most of water bodies are rich with iron oxides, neutral pH is not favorable for the adsorption of Cr(VI) [25]. This would be the probable reason for poor correlation among the  $Fe_{TSS}$  and  $Cr_{TSS}$  (Figure 8). High levels of  $Al_{TSS}$  shows availability of insoluble aluminium salts in TSS, and stability of these salts are high at neutral pH conditions [56]. Under this condition, aluminium containing minerals in TSS including hydroxide provides the best conditions for the fixation of Cr(VI) and Cr(III) [57] showing the richest relationship between  $Al_{TSS}$  and  $Cr_{TSS}$  compared to the relationship among  $Fe_{TSS}$  and  $Cr_{TSS}$  (Figure 8).





**Figure 8:** Correlation between; (a)  $Fe_{TSS}$  and  $Cr_{TSS}$ ; (b)  $Al_{TSS}$  and  $Cr_{TSS}$ ; (ii)  $Fe_{TSS}$  and  $Ni_{TSS}$  in suspended sediments

#### 4. Conclusions

The levels of Cd and Pb as dissolved forms are below the minimum detection limits in the surface water bodies studied. Difference between the acid extractable fraction and dissolved fraction of metals of Fe, Al, Mn, Cr, Cu and Zn are significant. Movement of trace metals with suspended solids (Cr, Cu, Zn and Ni) is not correlated with the loads of suspended solid for the period of interest. Contribution of acid extractable Fe and Al compounds for transportation of other trace metals (Cr, Cu, Zn and Ni) is very poor under the present catchment conditions.

#### 5. Acknowledgment

Quality and Innovation Grants (QIG) of Higher Education for Twenty First Century (HETC) - Window 3 funded by the World Bank is highly appreciated.

#### References

[1] W. Luo, T. Wang, Y. Lu, J.P. Giesy, Y. Shi, Y. Zheng, Y. Xing and G. Wu, "Multivariate and geostatistical analyses of metals in soils Landscape ecology of the Guanting Reservoir, Beijing", *Environmental Pollution*, vol. 146, pp. 567 - 576, 2007.

[2] B.J. Alloway, Ed., "Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability", Series: Environmental pollution, vol. 22, 3rd edition, Springer, 2013.

[3] J.J. Mortvedt, "Heavy metal contaminants in inorganic and organic fertilizers", *Fertilizer research*, vol. 43 (1-3), pp. 55-61, 1995/1996.

[4] O. S. Fatoki, and R. Awofol, "Levels of Cd, Hg and Zn in some surface from the Eastern Cape Province, South Africa", *Water SA*, vol. 29 (4), pp. 375-379, 2003.

[5] C. M. Haydar, N. Nehme, A. Awad, B. Koubaissy, M. Fakhri, A. Yaacoub, J. Toufaily, F. Villeras and T. Hamieh, "Assessing contamination level of heavy metals in the lake of Qaraaoun. Lebanon", *Eighth International Conference on Material Sciences*, 285 – 290, 2014.

[6] O. Akoto, T. N. Bruce and G. Darko, "Heavy metals pollution profiles in streams serving the Owabi reservoir", *African Journal of Environmental Science and Technology*, 2 (11), 354-359, 2008.

[7] G. Nordberg, B. Sandström, G. Becking and R.A. Goyer, "Essentiality and toxicity of trace elements: Principles and methods for assessment of risk from human exposure to essential trace elements", *J. Trace Elements in Exp. Med.*, vol. 13, 141-153, 2000.

[8] T. Hewawasam, "Effect of land use in the upper Mahaweli catchment area on erosion, landslides and siltation in hydropower reservoirs of Sri Lanka", *J. Natn. Sci. Foundation Sri Lanka*, Vol. 38 (1), pp. 3-14, 2010.

[9] S. Elakanda, Resource-based development: Experience from Mahaweli, Center for River Basin Organizations and Management (CRBOM), Solo, Central Java, Indonesia, 2010.

[10] H.M.P.L. Premarathne, G. M. Hettiarachchi and S. P. Indraratne, "Trace metal concentration in crops and soils collected from intensively cultivated areas of Sri Lanka", *Pedologist*, vol. 54 (3), 230-240, 2011.

[11] The Master plan (2012) Home page of Mahaweli Authority of Sri Lanka [Online]. Available: <http://www.mahaweli.gov.lk/The Master plan>.

[12] Rainfall data sheet, Aluthnuwara and Ulhitiya stations, year 2011, Meteorological department, 383, Bauddhaloka Mawatha, Colombo 07, Sri Lanka.

[13] World Health Organization (WHO), Investigation and Evaluation of Chronic Kidney Disease of Uncertain Etiology in Sri Lanka: Final Report (RD/DOC/GC/06), 2013.

[14] N. T.C. Athuraliya, T. D. J. Abeysekera, P. H. Amerasinghe, R. Kumarasiri, P. Bandara, U. Karunaratne, A. H. Milton, and A. L. Jones, "Uncertain aetiologies of proteinuric-chronic kidney disease in rural Sri Lanka", *Kidney International*, vol. 80, pp. 1212–1221, 2011.

- [15] K. P. Wanigasuriya, R. J. Peiris-John and R. Wickremasinghe, "Chronic kidney disease of unknown aetiology in Sri Lanka: is cadmium a likely cause? ", *BMC Nephrology*, vol.12 (32), doi:10.1186/1471-2369-12-32, 2011.
- [16] G.A.W. Wijesekara and B. Marambe, "Arsenic in the environment - an overview on global and Sri Lankan context", *Annals of the Sri Lanka Department of Agriculture*, vol.13, 229-243, 2011.
- [17] E. A. R. I. E. Siriwardhana, P. A. G. Perera, R. Sivakanesan, T. Abeysekera, and D. B. Nugegoda, "Could dietary water of chronic kidney disease of unknown etiology (CKDu) patients of Medawachchiya, Sri Lanka be a likely source for nephrotoxic agent?", *International Symposium on Water Quality and Human Health: Challenges Ahead-2014*, PGIS, University of Peradeniya, Sri Lanka, pp. 19, 2014.
- [18] H. A. Elliott, M. R. Liberati, and C. P. Huang "Effect of iron oxide removal on heavy metal sorption by acid subsoils", *Water, Air, and Soil Pollution*, vol. 27 (3-4), 379-389, 1986.
- [19] A. Violante, M. Ricciardella, and M. Pigna, "Adsorption of Heavy Metals on Mixed Fe-Al Oxides in the absence or Presence of Organic Ligands", *Water, Air, and Soil Pollution*, vol. 145 (1-4), 289-306, 2003.
- [20] R. Chandrajith, S. Nanayakkara, K. Itai, T. N. C. Aturaliya, C. B. Dissanayake, T. Abeysekera, K. Harada, T. Watanabe and A. Koizum, "Chronic kidney diseases of uncertain etiology (CKDu) in Sri Lanka: geographic distribution and environmental implications", *Environ Geochem Health*, vol. 33 (3), pp. 267-278, 2011.
- [21] J. M. R. S. Bandara, D. M. A. Senevirathna, D. M. R. S. V. Dasanayake, V. Herath, and J. M. R. P. Bandara, "Chronic renal failure in cascade irrigation systems in Sri Lanka associated with elevated dietary cadmium levels, rice and fresh water fish", vol. 30 (5), pp. 465-478, 2008.
- [22] A.E. Greenberg, L.S. Clesceri, E.D. Eaton, Eds., *Standard Methods for Estimation of Water and Waste Water*, 21st edition, American Public Health Association/American Water Works Association/Water Environment Foundation, Washington DC, 2005.
- [23] R.L. Rudnick, *The Crust*, vol. 3, Elsevier, 2005.
- [24] L. Friberg, G.F. Nordberg and V.B. Vouk, Eds., *Handbok on the toxicology of metals: Iron*, vol. 2, 2nd edition, Amsterdam, Elsevier, 1986.
- [25] R.B Mapa, S. Somasiri, and A. R. Dassanayake, Eds., *Soils of the Dry Zone of Sri Lanka: Morphology, Characterizations and Classification*, Soils Science society of Sri Lanka , 2010.
- [26] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Aluminum, ATSDR and the Environmental Protection Agency (EPA), USA, 2008.
- [27] World Health Organization (WHO), Aluminium in drinking water, WHO, Geneva, 1998.
- [28] C.T. Driscoll and W.D. Schecher, "The chemistry of aluminum in the environment", *Environmental Geochemistry and Health*, vol.12, 28-49, 1990.
- [29] W. van der Hoek, L. Ekanayake, L. Rajasooriyar and R. Karunaratne, "Source of drinking water and other risk factors for dental fluorosis in Sri Lanka ", *Int. J. Environ Health. Res*, vol. 13(3), pp. 285-93, 2003.
- [30] R.B. Mapa, S. Somasiri, and S. Nagarajh Eds., *Soils of the Wet Zone of Sri Lanka: Morphology, Characterizations and Classification*, Soils Science society of Sri Lanka , 1999.
- [31] R .B. Mapa, A. R. Dassanayake and H. B. Nayakekorale, Ed., *Soils of the Intermediate Zone of Sri Lanka: Morphology, Characterization and Classification*, Soils Science society of Sri Lanka, 2005.
- [32] V.H. Grassian, Ed, *Environmental Catalysis: Precipitation and Dissolution of Iron and Manganese Oxides*, CRC Press: Boca Raton, pp. 61- 81, 2005.
- [33] Environmental Protection Agency, United State (USEPA), Drinking Water Criteria Document for Manganese, *USEPA*, Office of Water, Washington, DC, 1994.
- [34] P. Alumaa, E. Steinnes, U. Kirso and V. Petersell, "Heavy metal sorption by different Estonian soil types at low equilibrium solution concentration", *Proc. Estonian Acad. Sci. Chem.*, vol. 50 (2), 104-115, 2001.
- [35] P. Loganathan, S. iganeswaran, J. Kandasami, and R. Naidu, "Cadmium Sorption and Desorption in Soils: A Review" *Critical Reviews in Environmental Science and Technology*, vol. 42 (5), 489-533, 2012.
- [36] J.M. Bandara, H.V. Wijewardena, Y.M. Bandara, R.G. Jayasooriya and H. Rajapaksha, "Pollution of River Mahaweli and farmlands under irrigation by cadmium from agricultural inputs leading to a chronic renal failure epidemic among farmers in NCP, Sri Lanka", *Journal of Environ Geochem Health*, Vol. 33 (5), 439-453, 2011.
- [37] L. Friberg, G.F. Nordberg and V.B. Vouk, Eds, *Handbook on the toxicology of metals*, 2<sup>nd</sup> edition , Amsterdam, Elsevier, pp. 664-679, 1986.
- [38] E. Helios-Rybicka, "Sorption of Ni, Zn and Cd on Sepiolite", *Clay Minerals*, vol. 20, 525-527, 1985.
- [39] United State Environmental Protection Agency (USEPA), *Effect of pH, DIC*,

- orthophosphate and sulfate on drinking water cuprosolvency* (EPA/600/R-95/085), Office of Research and Development, USEPA, DC., 1995.
- [40] W. Stumm, and J.J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, Chapter: Metal Ions in Aqueous Solution: Aspects of Coordination Chemistry, 3rd edition, New York: Wiley, 1996
- [41] D.G. Barceloux and D. Barceloux, "Copper", *Clinical Toxicology*, vol. 37, pp. 217-230, 1999.
- [42] L. Landner and L. Lindstrom, *Copper in society and in the environment: an account of the facts on fluxes, amounts and effects of copper in Sweden*. Vasteras, Swedish Environmental Research Group, 1999.
- [43] World Health Organization (WHO), International Program on Chemical Safety (IPCS), *Nickel*, WHO, Geneva, 1991.
- [44] H.I. Maibach, and T. Menné, Eds., *Human nickel exposure and chemobiokinetics*, Chapter: Nickel and the skin: immunology and toxicology, Boca Raton, FL, CRC Press, Inc., pp. 9-35, 1989.
- [45] F.C. Richard and A.C.M. Bourg, "Aqueous geochemistry of chromium: A review", *War. Res.*, vol. 52 (7), 807-816, 1991.
- [46] World Health Organization (WHO). Chromium in Drinking-water (WHO/SDE/WSH/03.04/04), Background document for development of WHO Guidelines for Drinking-water Quality, WHO, 2003.
- [47] A.M. Shiller and E.A. Boyle, "Variability of dissolved trace metals in the Mississippi River", *Geochimica et cosmochimica acta*, 51 (12), 3273 - 3277, 1987.
- [48] N. Masuda, S. Nakaya, H.R. Burton, and T. Torii, "Trace element distributions in some saline lakes of the Vestfold Hills, Antarctica", *Hydrobiologia*, vol. 34, 103-114, 1988.
- [49] A.G.P. Aravinna, N. Priyantha, H.M.T.G.A. Pitawala and S.K. Yatigammana, "Seasonal Variations of Water Quality of Downstream Catchment of River Mahaweli" *International Journal of Biological Sciences and Engineering*, 4 (4), 111 - 120, 2013.
- [50] F. A. Vega, E.F. Covelo and M. L. Andrade, "Competitive adsorption and desorption of heavy metals in mine soils: influence of mine soil characteristic", *J. Colloid Interf. Sci*, 298, 582-592, 2006.
- [51] T.K. Sen, S.P. Mahajan and K.C. Khilar, "Adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> on iron oxide and kaolin and its importance on Ni<sup>2+</sup> transport in porous media", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 211(1), 91-102, 2002.
- [52] M.B. McBride, "Cu<sup>2+</sup> adsorption characteristics of aluminum hydroxide and oxyhydroxides", *Clays and Clay Minerals*, vol. 30 (1), pp. 21-28, 1982.
- [53] D.C. Schroeder and G.F. Lee, "Potential transformations of chromium in natural waters", *War. Air Soil Pollut.*, vol. (4), 355-365, 1975.
- [54] R. Bartlett and B. James, "Behaviour of chromium in soils. III. Oxidation", *J. envir. Qua*, vol. 8 (1), 31-35, 1979.
- [55] L.E. Eary and D. Rai, "Kinetics of chromium(VI) oxidation to chromium(VI) by reaction with manganese dioxide", *Envir. Sci. Technol*, Vol. 21, 1187-1193, 1987.
- [56] C.T. Driscoll, "Aluminum in acidic surface waters: chemistry, transport, and effects", *Environ Health Perspect*, vol. 63, 93-104, 1985.
- [57] S. Musić, "Sorption of chromium(VI) and chromium(III) on aluminium hydroxide", *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 100 (1), pp. 185-196, 1986.