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Distribution and yield of trace metals from the foot of Mount Kilimanjaro to the coastal of Indian Ocean: impacts of natural and anthropogenic factors

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Abstract

Cases of water related diseases due to metal pollution are increasing over the global. The condition is serious to most of developing countries as a results of industrialization and population growth. Dissolved and particulate trace elements influence drinking water, aquatic ecosystem health and climate change. Mt. Kilimanjaro is one of the sources of water and icon in Africa but miss studies on dissolved and particulate metals. Therefore, this study was conducted to investigate geochemistry, distribution and yield of dissolved and particulate metals from Mt. Kilimanjaro to Indian Ocean. Surface water was sampled in rainy season and analyzed by high resolution inductively coupled plasma mass spectrometry in State Key Laboratory of Estuaries and Coastal Research. Health assessment revealed that level of Aluminium, iron, vanadium and Manganese in some stations were above recommended level, that can pose health impact to human and aquatic ecosystem. Correlation of Cobalt, Copper, Manganese and Vanadium with dissolved silicate, sulphate, calcium and dissolved organic carbon indicates that these elements were predominantly found in silicate, sulphide, carbonate and organic bounds. Positive relation between magnetic susceptibility with Copper and zinc reflects that magnetic susceptibility can be used as indicator of Copper and Zinc pollution. Rock weathering and anthropogenic activities were main sources of metals whereas redox reactions, pH, temperature and dissolved organic carbon were some of biogeochemical factors influencing level of metals. The basin transported more elements in particulate than dissolved form. Yield from Pangani River to Indian Ocean was lower than most of other rivers in East Africa.

River name	Discharge (m^3/s)	Area (km^2)	Al	Pb	V	Cr	Mn	Fe	Co	Ni	Cu
PRB (particulate)	15.1	43500	17.2 x10^3	54.2	236.1	22.7	16.0 x10^3	37.9 x10^3	71.1	617.7	163.6
PRB (dissolved)	15.1	43500	6.74	0.68x10^{-3}	0.12	6.11x10^{-3}	85.8x10^{-3}	4.33	2.96x10^{-3}	21.0x10^{-3}	19.0x10^{-3}
Gomati (dissolved)	351.8	30,437	1928 x10^3	1.6 x10^3	2.9 x10^3	1.74 x10^3	41.9 x10^3	758.2 x10^3	0.73 x10^3	2.5 x10^3	2.7 x10^3
Sabaki (dissolved)	72.6	69,900		1.11 x10^3		0.8 x10^3	22.4 x10^3			0.44 x10^3	

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Distribution and yield of trace metals from the foot of Mount Kilimanjaro to the coastal of Indian Ocean: impacts of natural and anthropogenic factors

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Key Points:

- Level of dissolved and particulate trace metals are increasing in developing countries with the increasing economic activities
- Most of rural communities rely on raw waters, high level of Fe, Al, V and Mn above recommended drinking level is alarming to water managers
- Temperature, pH, TSM, ions and altitude were some of the factors regulating partitioning of dissolved and particulate metals in Pangani

Abstract

Cases of water related diseases due to metal pollution are increasing over the global. The condition is serious to most of developing countries as a results of industrialization and population growth. Dissolved and particulate trace elements influence drinking water, aquatic ecosystem health and climate change. Mt. Kilimanjaro is one of the sources of water and icon in Africa but miss studies on dissolved and particulate metals. Therefore, this study was conducted to investigate geochemistry, distribution and yield of dissolved and particulate metals from Mt. Kilimanjaro to Indian Ocean. Surface water was sampled in rainy season and analyzed by high resolution inductively coupled plasma mass spectrometry in State Key Laboratory of Estuaries and Coastal Research. Health assessment revealed that level of Aluminium, iron, vanadium and Manganese in some stations were above recommended level, that can pose health impact to human and aquatic ecosystem. Correlation of Cobalt, Copper, Manganese and Vanadium with dissolved silicate, sulphate, calcium and dissolved organic carbon indicates that these elements were predominantly found in silicate, sulphide, carbonate and organic bounds. Positive relation between magnetic susceptibility with Copper and zinc reflects that magnetic susceptibility can be used as indicator of Copper and Zinc pollution. Rock weathering and anthropogenic activities were main sources of metals whereas redox reactions, pH, temperature and dissolved organic carbon were some of biogeochemical factors influencing level of metals. The basin transported more elements in particulate than dissolved form. Yield from Pangani River to Indian Ocean was lower than most of other rivers in East Africa.

1 Introduction

Rivers transport dissolved and particulate matters to the ocean; studies have shown that materials transported in the forms of suspended load and bed load exceed by a factor of 20 to that of dissolved and atmospheric dusts (Jickells et al., 2005; Walling, 2006). Therefore, most of metal elements whether coming from lithogenic or anthropogenic sources are transported in suspended form compared to that of dissolved form (Oelkers et al., 2011). Trace elements in dissolved form have direct impact to the drinking water whereas fluxes of trace elements in particulate form influence climate change (Hu et al., 2009; Wang et al., 2011) and coastal ecosystem (Wang et al., 2013).

Cases of water related diseases are increasing to most of developing countries (Reza & Singh, 2010). Factors such as industrialization and population growth, increase metal pollution to the surface and ground water (Cosgrove, & Loucks, 2015). In this case anthropogenic activities are considered as the major sources producing trace elements from point and non-point sources polluting riverine water which discharge to the coastal area (Zinabu, & Pearceet, 2003).

Metals pollution have attracted attentions due to their environmental persistence, toxicity, non-degradability and ability to accumulate in organs (Wang et al., 2013; Strady et al., 2017). Accumulation of metals in aquatic organisms can pass to human body through food chain leading to health effects (Ma et al., 2016). On the other hand, high level of trace elements is harmful not only to human being but also to aquatic organisms, for example Cd concentration above 0.1 µg/L can hinder reproductive process of some aquatic organisms (Tarvainen et al., 1997); Mn and Zn above 50 µg/L and 0.5 µg/L respectively, are harmful to freshwater fish such as trout (Sayer et al., 1989; Lydersen et al., 2002).

Tanzania is among of developing countries facing challenges of water quality for human and aquatic ecosystem health (Kihampa et al., 2013). It was observed that about 6 million people depend on water from Pangani River Basin (PRB) for drinking and other domestic activities (National Bureau of Statistics, 2013). However, from present knowledge only one metals pollution investigation was conducted in PRB with a focus on metals in sediments (Kihampa et al., 2014); as a result, understanding of the distribution, physical and chemical processes of metals in dissolved and particulate forms is limited. It should be well noted that composition of dissolved and particulate elements can give information such as source of the elements, intensity and condition of weathering (Tosiani et al., 2004). Since high quantity of trace elements are transported in particulate matter and partitioning of trace elements between dissolved and particulate phase can influence level of elements in the system. Therefore, to evaluate health risk in PRB and coastal area, it was important to study the concentration, distribution, physical and chemical processes of trace metals and yield of metals elements from the foot of Mt. Kilimanjaro to the coastal of Indian Ocean. Objectives of this study were to investigate potential sources and geochemical processes which control content and yield of dissolved and particulate trace elements from African continent such as Mt. Kilimanjaro to the coastal of Indian Ocean.

2 Study site

Pangani River Basin is an important basin in East Africa and mostly located in the southern part of Mt. Kilimanjaro and Meru (Figure 1). Most of the rivers originate on the slope of Mt. Kilimanjaro (5895 m asl), Meru (4565 m asl), Pare (2,462 m asl) and Usambara (2,280 m asl) (PWBO/IUCN, 2008). About 6 million Tanzanian depend on PRB for irrigation, tourism, mining, fishing, production of hydroelectric power and drinking (National Bureau of Statistic, 2013). Crops grown include sugar cane, sisal, coffee, maize, rice, coconuts, cassava and varieties of fruits. The basin experiences bimodal type of rainfall of which March-May as long rainy season whereas October-December as short rainy season (PWBO/IUCN, 2008). Large part of the basin is dominated by Usagaran metamorphic rocks whereas volcanic and sedimentary rocks are located in the northern and southern part, respectively (Selemani et al., 2018).

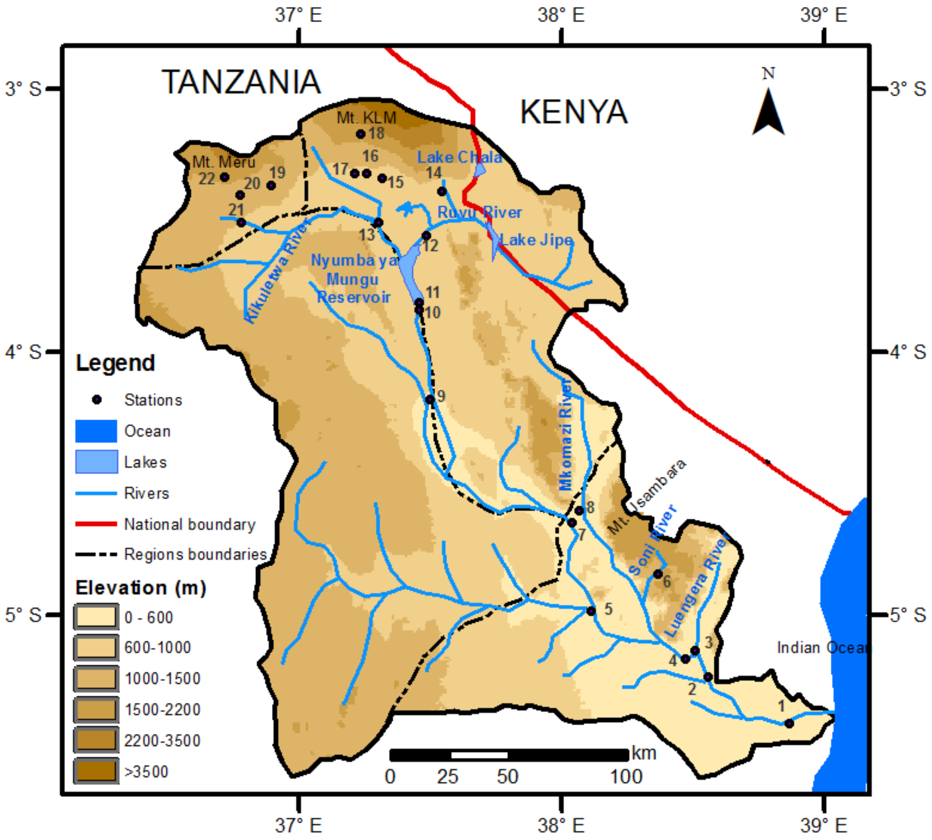

Figure 1. Study map showing sampling stations and elevation, 22 stations were sampled from river mouth to the foot of Mt. Kilimanjaro (KLM) and Meru.

3 Materials and Methods

22 surface water samples from rivers and lakes were collected in the rainy season of May 2015, during which mean rainfall was average about 750 mm whereas temperature was above average of 20 oC (TMA, 2015). These sampling stations covered the whole basin from source waters of Kilimanjaro Mountain to the river mouth (Figure 1). Stations were chosen based on

geomorphology of mainstream and watersheds of tributaries, weathering, water flow, landscape, as well as human activities so as to get ideal stations for the whole basin. In order to avoid anthropogenic disturbance along the river bank local boats were used to sample at the middle of the river and lakes. For trace element sampling, acid cleaned Nalgene bottles were attached to the end of a 5-m fishing pool and pole sampler were used on bow side of boat to sample at the middle of the river. Before sampling, the bottles were rinsed five times with river water and then filled. When the boat was not available, sampling was manipulated from river bank using the fishing pole and sampling bottle assembly (Zhang et al., 2015).

Whatman syringe filters (0.45 µm pore size) were used for filtration on-site in clean environment for dissolved and particulate elements including Pb, Al, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. To brief, the filtration was made wearing disposable plastic gloves in the upwind-side of open air to avoid local contamination. Before filtration, 5 ml of dilute HCl and then 10 ml Milli-Q were passed through to clean syringe and filter cartridge. The first 5 ml filtered water sample was used to flush filter. After filtration, the filtered water samples were kept in acid pre-cleaned 30 ml HDPE Nalgene bottles, kept in two plastic bags and stored in room temperature. Samples were then packed in ice box and transferred to State Key Laboratory of Estuarine and Coastal Research (Shanghai, China) for acidification to a 1.7-1.8 pH and analysis after a storage of at least one month for the dissolved metals. All the preparation work for stuffs used in sampling and analysis were conducted in the clean laboratory of East China Normal University.

The leachable particulate trace metals were conducted at room temperature involving Whatman filters following the method described in Buck et al. (2007). Diluted nitric acid at a pH≤2 was used in leaching experiment. Before leaching filters were dried at 60 ^{o}C; by using syringes, acid was injected in filters and left in filters for about 30 minutes to allow leaching to take place. New acids were pumped into the filters after every 30 minutes while the old acids from the filters were collected in pre-cleaned polyethylene bottle. The processes continued until a volume of about 5 ml was collected. The same digestion procedure was conducted for filters without particles to act as procedural blanks. Leaching process conducted in this paper is considered as partial extraction in some occasion concentration of trace metals in particulate form might be lower than concentration of particulate trace elements obtained from total digestion method (Fu et al., 2013).

High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS from Thermo Co.) was used in analysis of dissolved and leachable particulate trace metals. Standard solution of certified multi-elements from SPEX, USA together with purified nitric acid and high purity Milli-Q water (18.2 MΩ) were used to draw standard curve of 0, 0.1, 1, 10 and 96 ppb. Rh was used as an internal standard to monitor the variation of instrument sensitivity. Standard solution of 10 ppb was used for quality control of the instrument and was measured after every10 samples. The mean and standard deviation are shown in the first row of Table 1. Analysis of certified standard multi-elements solution showed that all values were within certified range.

Calculated precision was 1% for most of trace elements except V which was 2%, in general all values were within acceptable range.

Table 1. Measured standard solution of 10 ppb and R^2 values of standard lines (standard solution was prepared from certified multi-elements from SPEX, USA with purified nitric acid and high purity Milli-Q water).

Element	Pb	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Mean±SD	10.1±0.1	9.0±0.1	10.3±0.2	10.2±0.1	9.8±0.1	9.5±0.1	10.1±0.1	10.7±0.1	10.4±0.1	11.9±0.1
R^2 of standard line	0.999	0.999	1.0	0.999	1.0	0.999	1.0	0.999	1.0	0.999

Electrical conductivity, temperature, pH, dissolved oxygen and salinity were measured in the field with Multi-parameter probe (Multi 350i Set 5 model from WTW, Weilheim, Germany). The pH meter was calibrated by buffer solution of pH 4.01and 7.00 whereas dissolved oxygen meter was calibrated by saturated air with water vapour. Selemani et al. (2017a) described the detail of sampling and analysis of inorganic nutrients (dissolved silicates) in which a SkalarSANplus continuous flow autoanalyzer was used in measurement. Some samples were chosen to test quality of the data by analyzing in triplicate calculated precision was <5%. A Shimadzu Total Organic Carbon (TOC) analyser (model: TOC L-CPH) was used to analyze dissolved organic carbon (DOC) by the method described in Wu et al. (2007). Other data including major ions, magnetic parameters and stable water isotopes (δ^{18}O and δ^{2}H) which was used in data interpretation were obtained from articles published in peer-reviewed journal (e.g. Selemani et al., 2017b, Mzuza et al., 2017).

4 Results

4.1 Trace elements from source water to the river mouth

Mean content of each element together with their range are presented in Tables 2. Concentration of metals in both dissolved and particulate forms varied widely from upstream to river mouth. Concentration of almost all elements increased downward on the slope of Mt. Kilimanjaro, Meru and Usambara. Almost, all elements their concentrations in dissolved form were below recommended drinking water standards except V, Mn and Al in few stations.

Among of the sampling stations elements Pb, Cr, Co, Ni, Cu and Zn did not vary over long range while other elements including Al, V, Mn and Fe varied over long range (Table 2). Tributaries from Mt. Kilimanjaro pour their trace elements into the reservoir via station 12 whereas trace elements from Mt. Meru enter into the reservoir via station 13 (Figure 1). Concentration of all dissolved and particulate trace elements from Mt. Meru were higher than trace elements from Mt. Kilimanjaro. Input of trace metals from Mt, Usambara enter the main Pangani River through Soni and Luengera Rivers (station 6 and 3, respectively). Most of trace metals (dissolved and particulate) from Mt. Usambara to the main Pangani River were lower than input from Mt.

Kilimanjaro and Mt. Meru. Different levels of trace elements have been contributed by petrology and rate of weathering. PRB has igneous rocks in upstream and metamorphic rocks in downstream (PWBO/IUCN, 2008). Rate of weathering was lower in metamorphic rocks compared to that of igneous rocks (Selemani et al., 2017b).

Trend of trace metals from the reservoir to river mouth was illustrated in Figures 2 and 3. Concentration of almost all dissolved trace metals (except Al) decreased from the reservoir to river mouth (Figure 2a). On the other hand, concentration of all trace metals in particulate form increased from the reservoir to river mouth (Figure 3).

Upstream stations including station 18 located on tributaries from Mt. Kilimanjaro whereas station 22 and 19 located on tributaries from Mt. Meru both had lowest level of most trace elements in dissolved and particulate form. In this case concentration of trace elements in dissolved and particulate form was low in upstream stations of Mt. Meru and Kilimanjaro while on the foot of those Mountains concentration increased before the reservoir. Generally, PRB has low rate of weathering; additionally, low rate of weathering and anthropogenic activities in upstream reduced level of trace elements whereas opposite was the case on the foot of Mt. Kilimanjaro and Meru increasing level of trace elements (Selemani et al., 2017b).

4.2 Comparison between dissolved and particulate trace elements

Concentration of all elements was higher in particulate than dissolved form (Table 2). Highest level of dissolved Al, Mn and Fe was 616, 490 and 395 µg/L, respectively. Highest level of Al and Fe were measured at station 1 which was located in river mouth on the other hand Mn was measured at station 8 located on the slope of Mt. Usambara. Highest level of particulate Al, Mn and Fe were 9.41×10^3, 7.23×10^3 and 4.46×10^3 µg/g, respectively. Highest level of Al was measured at station 19 located on the slope of Mt. Meru whereas Mn and Fe were measured at station 8 located on the slope of Mt. Usambara. Partition coefficient (K_d) was used to compare concentration of particulate and dissolved trace elements. The partition was estimated based on the method describe by Feng et al. (2017).

$$K_d=C_p/C_d$$

where C_p was concentration of metals in particulate (µg/g), C_d was concentration of metals in dissolved form (µg/L). This coefficient is an important method in assessing pollution impacts and geochemical processes taking place during transport of trace elements in a solid-solution interfere (Fu et al., 2013). Nevertheless, partition coefficient (K_d) is not a true equilibrium coefficient but empirical term which change depending on various factors such as dissolved organic carbon (DOC), total suspended matter (TSM), dissolved ions, temperature, pH among others (Hatje et al., 2003). The effects of altitude on the phase transfer of trace metals was also investigated and illustrated in figure 4. Variation of partition coefficient with elevation showed negative relation except chromium (Figure 4d). Among all trace elements Mn had the highest K_d values and V had the lowest K_d values see figure 4e and 4c.

Figure 5 shows relationship between partition coefficients (K_d) with TSM. Positive relation was observed for almost all trace elements except nickel (Figure 5h). In addition to that positive relation (although statistically not significant) was observed between most of trace elements and TSM (Table 3). In this case TSM in PRB can be used as indicator of trace elements in the basin.

Since level of trace elements in particulate form increased with the decreasing altitude, flux of trace elements to Indian Ocean was higher in particulate form than dissolved form (Table 4).

4.3 Comparison between different elements

Order of abundance was Al>Fe>Mn>V>Ni>Cu>Zn>Cr>Co>Pb for dissolved phase and Al>Fe>Mn>Zn>Ni>Cu>V>Co>Cr>Pb for particulate fraction. Most of elements in the earth crust are Al, Fe and Mn. On the other hand, Pb was the least element in the list and earth crust. Therefore, these trends mostly coincide with geochemical distribution of these elements in the earth crust. Close observation of Figures 2 and 3 shows that distribution of those elements was not uniform from the reservoir to river mouth similar case occurred from upstream to reservoir reflecting that either rate of weathering was not uniform or there was addition input from other contribution such as anthropogenic sources.

Table 2. Dissolved trace metal (µg/L) and Leachable particulate metal (µg/g) given in mean±SD and range (in parentheses), and compared with other tropical rivers and global average, mean weight of metals in sediment were given in µg/g

River	Country	Pb	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	References
PRB (dissolved)	Tanzania	0.03±0.03 (0.01-0.1)	143±182 (3.6-616)	9.52±7.3 (0.05-21.5)	0.27±0.6 (0.02-2.6)	30.27±42 (0.05-490)	112.7±138 (0.7-395)	0.14±0.2 (0.01-0.58)	1.11±0.7 (0.32-3.19)	0.92±0.9 (0.04-3.86)	0.54±1.2 (0.02-5.56)	This study
Warri River	Nigeria	30			70	155	1050	30	30	30	190	Ama et al., 2017
Sabaki	Kenya	34			24	902.3			13.5		85.4	Muiruri et al., 2013
Bonny River	Nigeria	0.23			1.39		1.36	0.24	0.22	0.47	2.81	Onojake et al., 2017
Gomati River	India	4.3	5289	8.21	4.76	115	2080	2	7	7.34	16.9	Jigyasu et al., 2015
World averaged		0.08				34.7	66			1.45	0.61	Shulkin, & Zhang, 2014
Leachable particulate and sediment metals												
PRB (particulate)	Tanzania	2.02±5 (0.13-24)	1855±3983 (15-9410)	7.86±12 (0.01-22)	1.82±6 (0.01-7)	839±1694 (20-7237)	1103±1585 (45-4464)	3.69±5.62 (0.03-20)	12.2±18 (0.02-23)	10.6±19 (0.12-33)	23.3±81 (0.04-86)	This study
PRB (Sediment)	Tanzania	21.5		148.5	72	1350		26.5	36.5	46	225	Kihampa et al., 2014
Cay River	Vietnam	62.7	0.092	88.5	90.2	0.05	0.03	68.4	153	105	79.8	Koukina, & Lobus, 2019
Sorocaba River	Brazil				61			18	24	28	252	Fernandes et al., 2016
World averaged		25	0.09	120	85	0.001	0.05	19	50	45	130	Savenko, 2006

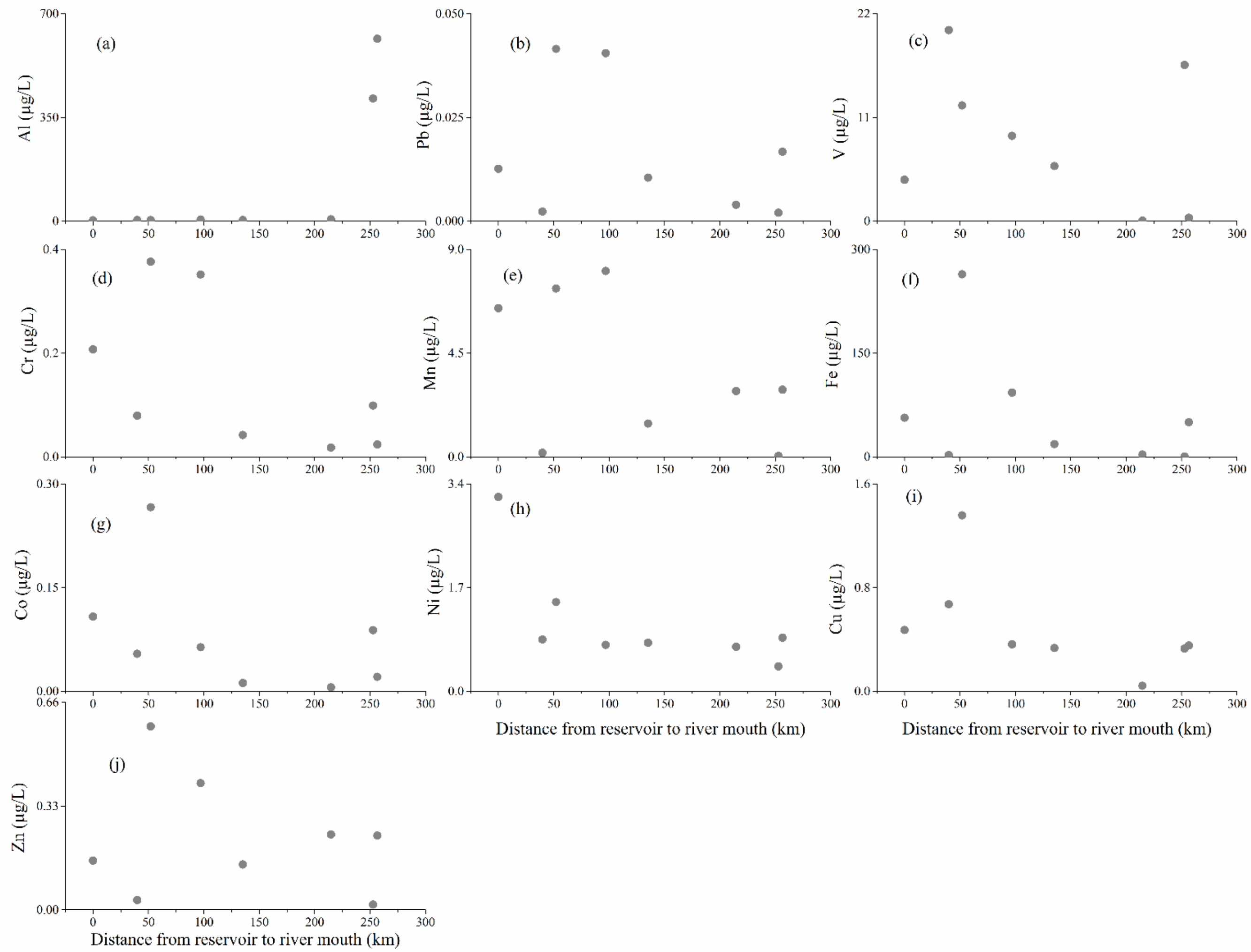

Figure 2. Level of dissolved elements from the reservoir (station 10) to river mouth (station 1), almost all elements decreased from reservoir to river mouth except Al.

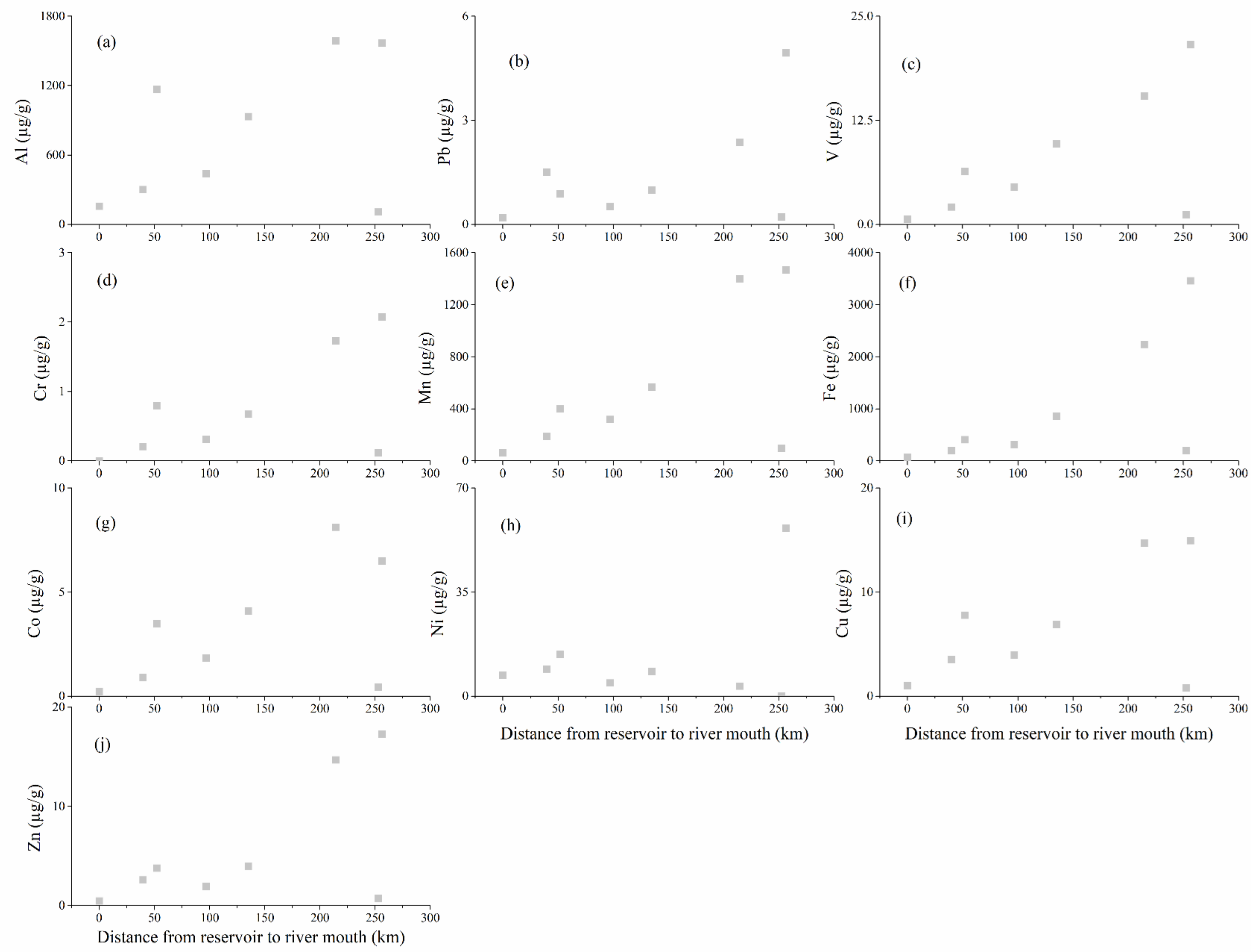

Figure 3. Level of particulate elements from the reservoir (station 10) to river mouth (station 1), all elements increased from reservoir to river mouth.

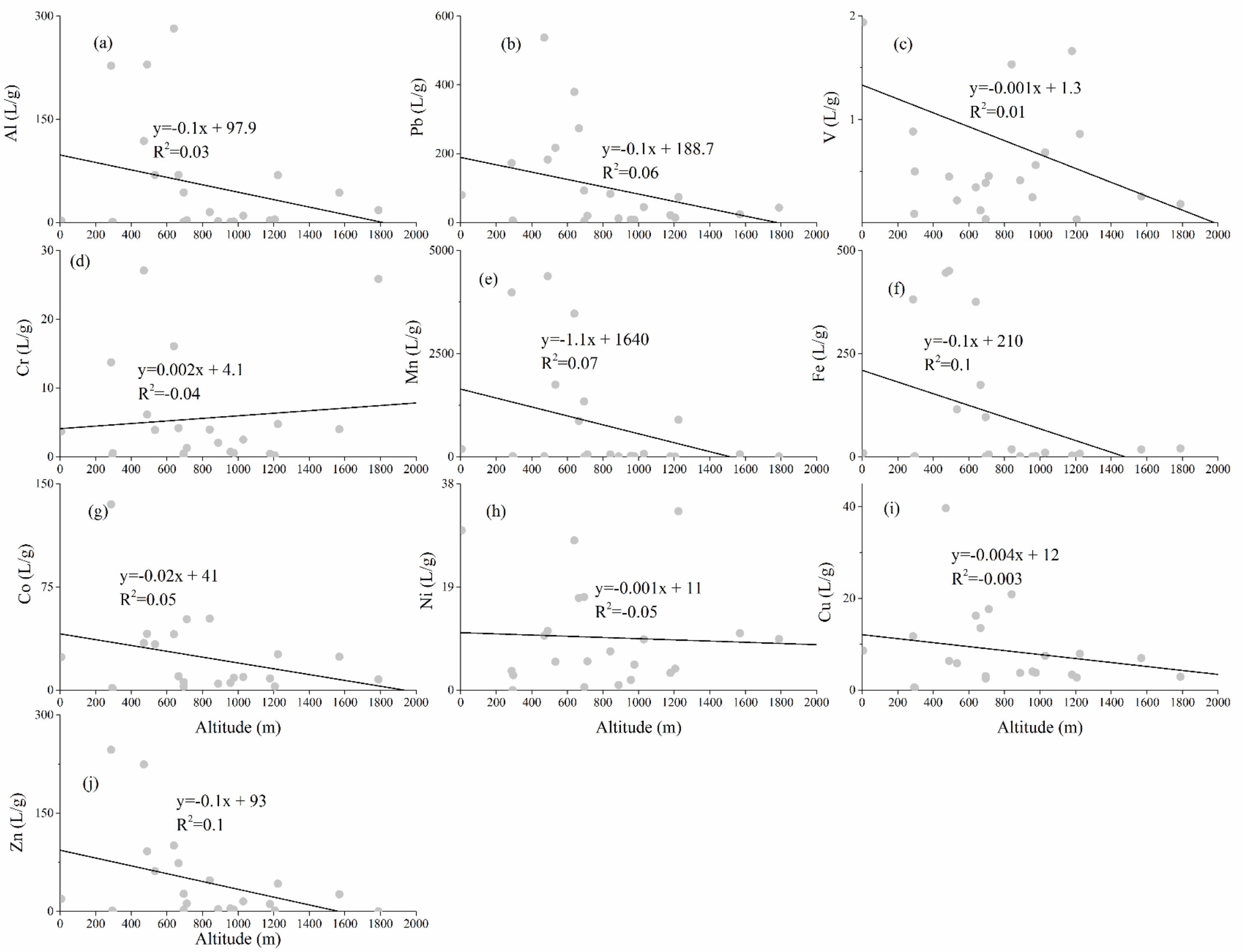
(a)
Al (L/g)
300
150
0
y=-0.1x + 97.9
R^2=0.03
(b)
Pb (L/g)
600
400
200
0
y=-0.1x + 188.7
R^2=0.06
(c)
V (L/g)
2
1
y=-0.001x + 1.3
R^2=0.01
(d)
Cr (L/g)
30
20
10
0
y=0.002x + 4.1
R^2=-0.04
(e)
Mn (L/g)
5000
2500
0
y=-1.1x + 1640
R^2=0.07
(f)
Fe (L/g)
500
250
0
y=-0.1x + 210
R^2=0.1
(g)
Co (L/g)
150
75
0
y=-0.02x + 41
R^2=0.05
(h)
Ni (L/g)
38
19
0
y=-0.001x + 11
R^2=-0.05
(i)
Cu (L/g)
40
20
0
y=-0.004x + 12
R^2=-0.003
(j)
Zn (L/g)
300
150
0
y=-0.1x + 93
R^2=0.1
0 200 400 600 800 1000 1200 1400 1600 1800 2000
Altitude (m)

Figure 4. Ratio of particulate/dissolved elements from low altitude to high altitude, the ratio decreased with the increasing altitude.

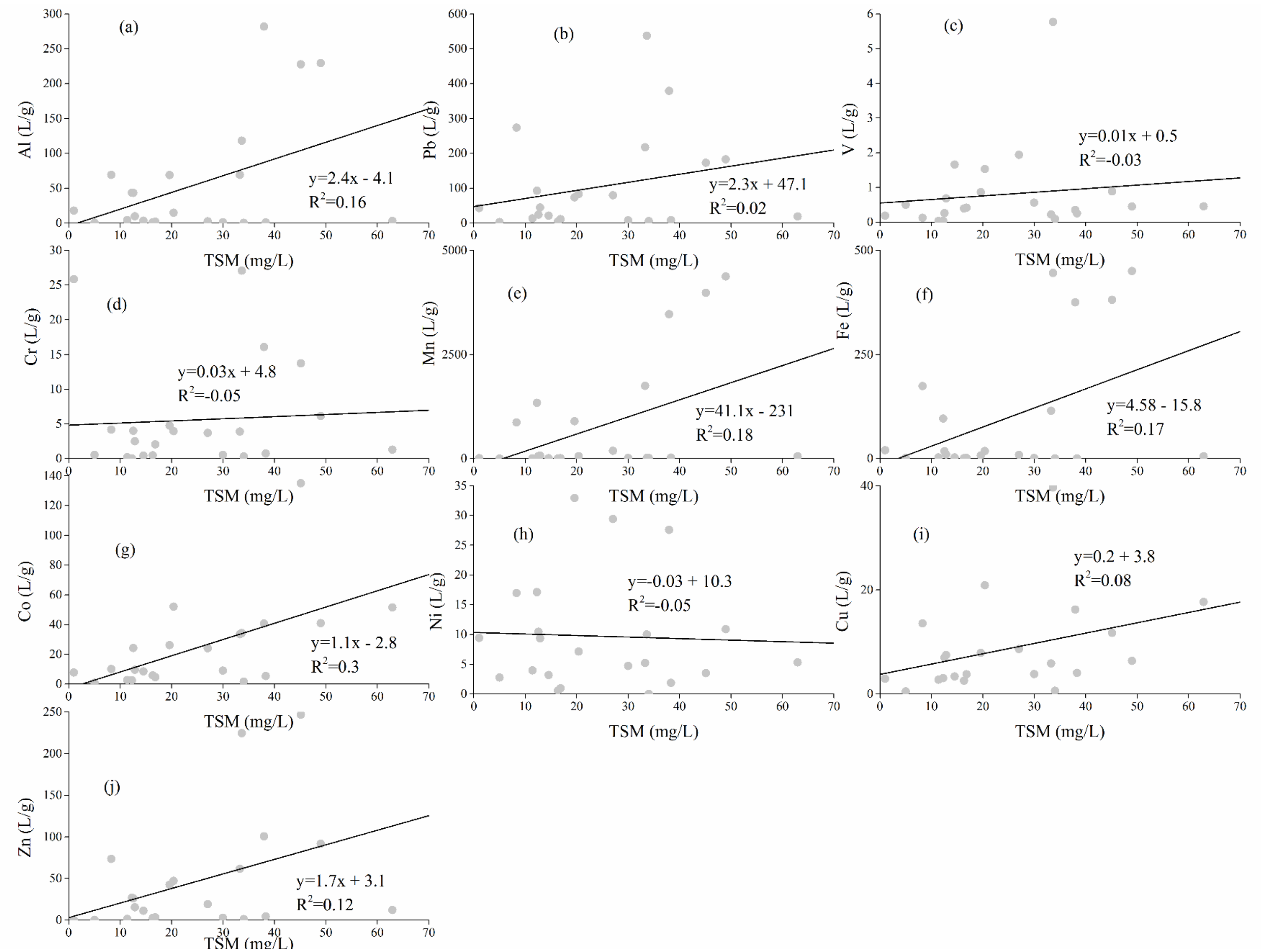

Figure 5. Variation of ratio of particulate and dissolved trace metals against total suspended matter; the ratio increased with TSM.

Table 3. Correlation matrix of metals and other influencing factors. DO was dissolved oxygen and XLF was magnetic susceptibility.

(**. Correlation is significant at the 0.01 level (2-tailed); *. Correlation is significant at the 0.05 level (2-tailed).

	Pb	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	DOC	Temp	pH	DSi	SO_4^{2-}	HCO_3^-	Ca	DO	XLF
Pb																			
Al	0.82**																		
V	-0.07	-0.05																	
Cr	0.73**	0.51*	0.20																
Mn	-0.12	-0.15	-0.18	-0.07															
Fe	0.38	0.63**	-0.13	0.22	-0.08														
Co	0.36	0.36	0.10	0.55**	0.69**	0.36													
Ni	0.28	0.37	-0.18	0.31	0.34	0.34	0.57**												
Cu	0.41	0.40	0.35	0.45*	-0.02	0.57**	0.41	0.11											
Zn	0.77**	0.48*	0.13	0.95**	-0.08	0.19	0.46*	0.18	0.53*										
DOC	-0.11	0.05	0.58**	0.01	0.26	0.35	0.40	-0.09	0.67**	-0.02									
Temp	-0.08	0.12	0.66**	0.05	0.17	0.24	0.41	0.12	0.13	-0.11	0.51*								
pH	0.05	0.05	0.60**	0.15	-0.19	-0.04	0.05	-0.33	0.34	0.14	0.44*	0.48*							
DSi	0.09	0.02	0.47*	0.32	-0.25	-0.11	0.02	0.32	0.17	0.28	0.05	0.10	0.25						
SO_4^{2-}	0.02	0.05	0.89**	0.32	-0.16	0.11	0.29	-0.13	0.42	0.21	0.64**	0.73**	0.58**	0.31					
HCO_3^-	-0.17	-0.13	0.90**	0.08	0.19	-0.08	0.34	-0.11	0.39	0.02	0.77**	0.73**	0.53*	0.29	0.86**				
Ca	0.05	0.01	0.12	0.25	0.89**	-0.02	0.87**	0.37	0.16	0.17	0.42	0.38	0.04	-0.07	0.23	0.44*			
DO	-0.02	-0.14	0.02	0.01	-0.46*	-0.37	-.49*	-0.5*	-0.08	0.08	-0.15	-0.38	0.30	0.10	-0.09	-0.19	-0.46*		
XLF	0.19	0.08	-0.03	0.37	-0.14	0.17	0.11	0.29	0.44*	0.45*	0.08	-0.36	0.05	0.65**	-0.05	-0.09	-0.06	0.12	

Table 4. Yield of trace elements (g/year/km2) from PRB to the coastal of Indian Ocean and compared with other tropical rivers.

River name	Discharge (m^3/s)	Area (km^2)	Al	Pb	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
PRB (particulate)	15.1	43500	17.2 x10^3	54.2	236.1	22.7	16.0 x10^3	37.9 x10^3	71.1	617.7	163.6	189.3
PRB (dissolved)	15.1	43500	6.74	0.68x10^{-3}	0.12	6.11x10^{-3}	85.8x10^{-3}	4.33	2.96x10^{-3}	21.0x10^{-3}	19.0x10^{-3}	9.9x10^{-3}
Gomati (dissolved)	351.8	30,437	1928 x10^3	1.6 x10^3	2.9 x10^3	1.74 x10^3	41.9 x10^3	758.2 x10^3	0.73 x10^3	2.5 x10^3	2.7 x10^3	6.2 x10^3
Sabaki (dissolved)	72.6	69,900		1.11 x10^3		0.8 x10^3	22.4 x10^3			0.44 x10^3		2.8 x10^3

5 Conclusions

5.1 Mechanisms influencing transport of trace metals

Spatial variation of trace elements (particulate/dissolved form) is influenced by several factors among them are magnetic properties, ions, geo-chemical processes and anthropogenic activities. In addition to that, since sampling occurred in rainy season possibly dilution and weathering contributed by rainfall might also played roles in the spatial variation of trace elements. Magnetic susceptibility is the variable which reflects concentration of magnetic minerals. High values of magnetic susceptibility means high magnetic minerals and vice versa. Magnetic susceptibility analyzed from sediment in PRB was found to increase in the order of Mt. Meru> Mt. Kilimanjaro> Mt. Usambara> main river (Mzuza et al., 2017). High level of magnetic susceptibility can be contributed by anthropogenic input including industrial activities and traffic exhaust (Lu et al., 2007). Most of stations in PRB are located along roadside; in addition to that some stations on the slope of Mt. Meru are located downstream Arusha city. There is high chance that high level of magnetic susceptibility in stations located on the slope of Mt. Meru was contributed by anthropogenic input (Lu et al., 2007). Positive correlation between Magnetic susceptibility with Cu and Zn reveals either these elements were incorporated or adsorbed on magnetic materials (Table 3). This relation suggests that Cu and Zn likely to come from anthropogenic input. Magnetic materials can also be used as indicator of Cu and Zn pollution in the basin.

Mn was the element with highest K_d values, and high values signify greater affinity of Mn to be associated and transported in SPM. In this results Mn was strongly bound by SPM whereas V with lowest K_d values was mostly transported in dissolved form. Strong positive correlation between V and DOC shows there was formation of complex which played role to transport V in dissolved form (Table 3). Low K_d were also observed in Cu in which positive correlation between Cu and DOC also support that Cu formed stable complexes with dissolved organic ligands causing high concentration of Cu to be transported in dissolved form (Table 3; Figure 4i; Fu et al., 2013).

Variation of partition coefficient with elevation showed negative trend in almost all trace elements except Cr (Figure 4d). Negative relation reflects that increasing dissolved trace elements decreases concentration of trace elements in particulate form. The rate was higher in Mn than other elements bear in mind that Mn is among of major elements in the earth crust and low rate was observed in Ni and V (Figures 4 c, e and h).

Increasing level of TSM led to the increasing level of trace elements in particulate form (Figure 5). Mn had higher rate compared to other elements whereas lower rate than other elements was observed in V (Figure 5c and e). Since TSM arise from weathering, increasing rate of weathering lead to the increasing concentration of trace elements in particulate form. These trend could be contributed by decreasing concentration of dissolved trace elements and increasing concentration of particulate trace elements (Figures 2 and 3). Increasing trace elements in particulate form and decreasing trace elements in dissolved form could be caused by several factors. For example, normally there is competition between anion and cations in water either to form anion complexes such as Cd-chloro-complexes which increase concentration of dissolved fraction. Opposite is the case for cations which help for sorption to occur on SPM increasing level of metals in particulate form (Fu et al., 2013). The condition was supported by previous study which showed that concentration of particulate organic carbon and total suspended matter increased with decreasing altitude (Selemani et al., 2018). Study from Selemani et al. (2017b) also showed increasing concentration of cations with decreasing elevation. Increasing concentration of TSM, particulate organic carbon and cations can enhance sorption to occur in this case trace elements attach on particles' surfaces increasing concentration of trace elements in particulate form.

Another possible cause of increasing concentration of trace elements in particulate form compared to that of dissolved metals was microbial uptake. Waters in PRB are shallow and flow at low speed for example discharge measured at river mouth was 15.1 m^3/s (Selemani et al., 2017a). Low speed can allow microbial uptake of dissolved trace elements decreasing level of trace elements in dissolved phase (Molander, 2015).

Water pH is another factor influencing sorption of trace elements on particulate matter. PRB has pH ranging from 6.4 to 8.8 with average of 7.9 (Selemani et al., 2017a). High pH (alkalinity condition) combining with high level of particulate matter bear in mind that sampling occurred in rainy season can enhance sorption to occur increasing level of trace elements in particulate form compared to those in dissolved form (Shulkin, & Zhang, 2014).

Concentration of metals varied from one station to the other, large standard deviation signifies that there was wide variation between stations (Tables 2). Wide range is common phenomena to most of rivers in developing countries due to geo-chemical processes and anthropogenic stress which can either speed up weathering or add metals directly to the rivers (Zinabu, & Pearce, 2003). For example, station 18 located at highland in forest reserve of Mt. Kilimanjaro had 0.004 µg/L concentration of Pb whereas station 12 located at lowland near the reservoir had 0.03 µg/L concentration of Pb. Therefore, low level of metals in upstream stations was contributed by low/no anthropogenic impacts since some of the stations located in reserved areas whereas addition of metals from anthropogenic input increased level of metals in downstream stations. Slope of the basin might be another reason played role to decrease level of metals in upstream compared to that of downstream. On one hand, steep slope in upstream slow rate of weathering reducing input of metals from rocks. On the other hand, gentle slope downstream increased rate of weathering increasing level of dissolved and particulate metals released from rocks.

Level of metals both in dissolved and particulate form followed abundance of those metals in the earth crust. The condition suggest that, most of the metals came from natural sources compared to other sources. Trend of metals both dissolved and particulate form increased from upstream to downstream also give possibility of coming from the same source. Adopting published data on the level of trace elements in sediments conducted by Kihampa et al. (2014); comparison on the level of metals in dissolved, particulate and sediments the results showed that the level of metals were higher in sediments compared to other compartments, sediments was the major sink of metals in PRB (Kihampa et al., 2014; Tables 2). Long residence time of trace elements in sediments can reflect history of pollution in a given area (Tuna et al., 2007). Nevertheless, temporal variation of trace elements can be investigated in dissolved and particulate form. Therefore, observed high concentration of trace elements in sediments can be contributed by high residence time of those elements in sediment. Several studies elsewhere have also revealed lower concentration of metals in dissolved than in particulate and sediment (Jaishankar et al 2014; Javed, & Usmani, 2017).

Comparison on the level of metals in PRB with some other tropical rivers; the results showed that level of metals in PRB was lower than Sabaki and Warri Rivers (Muiruri et al., 2013; Ama et al., 2017). The level in PRB was comparable to Bonny and global average (Onojake et al., 2017; Shulkin, & Zhang, 2014). Sabaki and Warri Rivers were influenced by mining and industrial activities whereas Bonny had minimum anthropogenic input. Average dissolved concentration of Ni in PRB was higher than global average whereas levels of Cu and Co were lower than global average, respectively (Chester, & Jickells, 2012).

Redox reaction was one of biogeochemical processes which influenced level of Mn, Co and Ni in PRB. Negative correlations between these metals with dissolved oxygen (DO) suggest that decreased DO increased level of Mn, Co and Ni (Table 3). In this phenomenon dissolved Mn, Co and Ni precipitated to form insoluble metals with the increase of DO (Fuller, & Harvey, 2000). Opposite was the case when level of DO decreased. High level of dissolved Mn was also observed in springs sampled around Lake Victoria in East Africa, authors revealed that redox reaction under acidic condition was among of the factor increased level of Mn (Bakyayita et al., 2019).

Charge ion was another factor influencing level of V in PRB. Increasing electrical conductivity speeded up weathering leading to the increasing level of V (Table 3). This means desorption of V from the rocks increased with charge ions. Station 5 recorded highest level of electrical conductivity (472 µS/cm), and was the one recorded highest level of dissolved V (21.5 µg/L). Similarly, pH had positive relation with V (Table 3). Such relation can result from variation in the amount of V from different rocks source or chemical in nature (Elbaz-Poulichet et al., 1999). Alkaline pH with high level of negative charge attracted positive charges V speeding adsorption of V from rocks and other sources (Gurumurthy et al., 2014). Opposite was the case in acidic pH. Level of V in PRB was also influenced by temperature. The increase in temperature speeded up rate of weathering increasing level of V in water (Tripti et al., 2013).

Cu and V had positive correlation with DOC (Table 3). This means level of Cu and V were influenced with the concentration of dissolved organic carbon (DOC). Organic ligands normally form complexes with Cu and V (Elbaz-Poulichet et al., 1999). In this case formation of complexes speed up dissolution of Cu and V from particulate/sediment increasing level of dissolve Cu and V.

Strong positive relation between Ca with Mn and Co indicates similar behavior and the same carbonate source (Table 3). The basin is dominated by carbonate weathering compared to silicate weathering (Selemani et al., 2017b). Weathering in carbonate minerals released Ca together with Mn and Co.

Presence of gypsum/pyrite in the basin increased level of SO_4^{2-} especially downstream (Selemani et al., 2017b). Strong Positive SO_4^{2-}-V and weak positive SO_4^{2-}-Co correlation reflect similar characteristics and similar source from pyrite/gypsum weathering (Elbaz-Poulichet et al., 1999).

Particulate trace elements especially Al, Mn and Fe in PRB was higher than other rivers and global average (Table 2). High concentration of mentioned elements was likely to be contributed by mafic rocks which dominated the basin. Low level of Pb compared to global average was contributed by low anthropogenic input (Table 2).

5.2 Potential sources of metals

To investigate potential sources of trace elements; enrichment factor (EFs) was used as an index of environmental contamination. Silicon (Si) is the most abundant elements in the earth crust and it is conservative; in water dissolved silicate (DSi) is considered to come from natural sources. Therefore, concentration of DSi reflects contribution from natural sources. Due to its conservative nature Si was used in the normalization. Enrichment factor was estimated as follows

$$EFs=(M/DSi)_{dissolved}/(M/DSi)_{rock}$$

Where M was the content of the element concern in dissolved and in rock. Concentration of element in rocks was reference content which was adopted from Taylor, & Mc Lennan (1985). This is the weight in the earth crust. The basin is dominated by volcanic rocks from Mt. Kilimanjaro and Meru in this case mean andesitic weight of the upper earth crust was considered as reference weight (Selemani et al., 2017b).

Finding showed that almost all station the ratio was less than 1 exceptional occurred in one station in which ratio of Mn was higher than 1 the station was located on the slope of Mt. Usambara (Figure 6c).

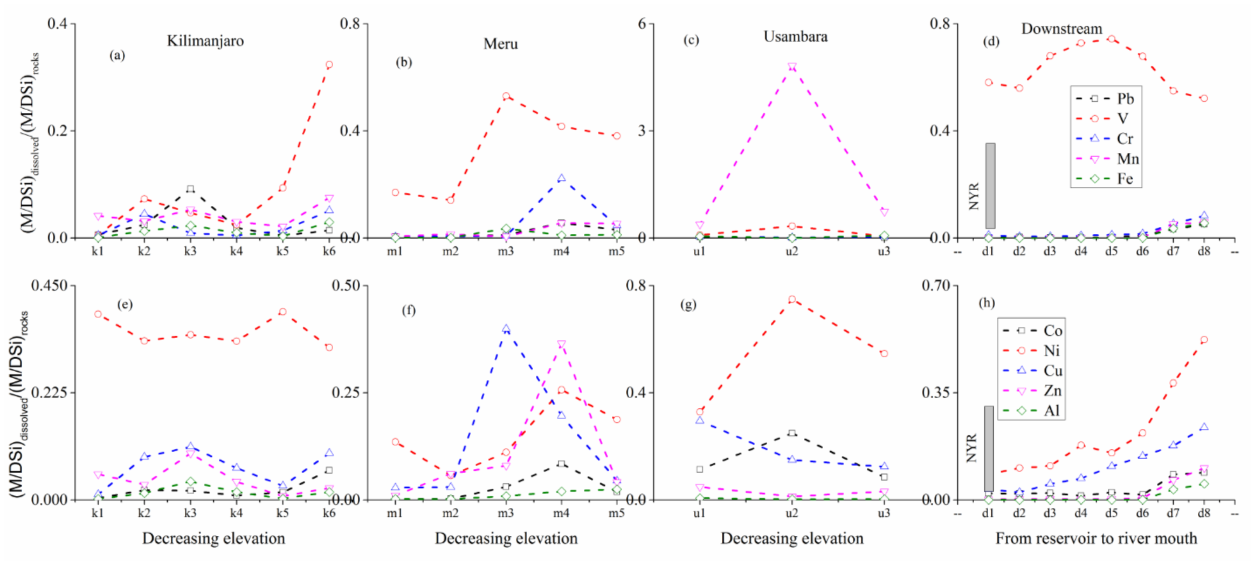

Figure 6. Weight of the dissolved metals to that of DSi and weight in the rocks. Figure shows stations on the slope of Mt. Kilimanjaro, Meru, Usambara and from Nyumba ya Mungu (NYR) to river mouth.

Low enrichment factor signify that based on this method most of the trace elements originated from natural sources basically from rock weathering. Furthermore, low enrichment factor suggests that rate of weathering of those trace elements were lower than that of DSi.

In water Mn mainly comes from natural sources such as rock weathering. Dissolution of Mn increases with the decrease of dissolved oxygen at low pH. Measured low level of DO on the slope of Mt. Usambara played role in increasing level of Mn. Concentration of Mn on the slope of Mt. Usambara cannot be considered to come from anthropogenic activities since there was no either industrial activities, dry cell batteries waste or emission from welding (Javed and Usman 2017). High level of Mn and Fe were also observed in springs sampled around Lake Victoria basin (GIBB, 1998). Since PRB and Lake Victoria are located in Eastern Africa, there is high chance that the soils and rocks in this region are rich in Mn and Fe (Bakyayita et al., 2019).

Factor analysis is another method which can be used to investigate sources of elements. Factor analysis was conducted and the results are presented in table 5 and 6 for dissolved and particulate fractions, respectively. The first three factors were chosen (1-3); contribution of 72.8% was considered as enough to explain dominant sources of metals in the basin. The first factor was dominant accounted for 38.9%, in the order of magnitude contribution of the elements Cr, Pb, Zn, Al, Co, Cu and Fe was higher in the first factor than other factors. High contribution means that the occurrence and concentration of these elements were the most influential in the percentage (Table 5).

Table 5. Factor matrix for dissolved trace elements.

Factors	1	2	3

Cr	0.852	-0.154	
Pb	0.842		-0.396
Zn	0.831	-0.198	
Al	0.783		-0.399
Co	0.69	0.371	0.582
Cu	0.678	-0.399	0.27
DSi		0.736	-0.415
Mn		0.674	0.658
V	0.105	-0.659	0.45
Ni	0.483	0.587	0.149
Fe	0.59		-0.135
Eigenvalues	4.279	2.145	1.58
Contribution rate (%)	38.903	19.5	14.364
Accumulated contribution rate (%)	38.903	58.403	72.767

It was observed earlier that concentration of Al was higher than all other metals in the basin. From the idea that Al is higher in the earth crust than other elements and presence of Fe in the first component relate to the influence of mafic rocks in the composition of trace elements in the basin.

It is well known that Pb has high health impact in which WHO recommends not taking more than 10µg/L (WHO, 2011). Excessive Pb can decrease fertility and cardiovascular diseases. Main possible source of Pb are anthropogenic sources including metal workshops, wearing parts of vehicles, scrap yards and motor services center (Bakyayita et al., 2019). On one hand, highest level of dissolved Pb was 0.12 µg/L measured downstream Mt. Meru at station 21 which collects water from Arusha City. Anthropogenic activities such as metal workshops, motor vehicle service centers and scrap yards are common in Arusha City. On the other hand, Pb at station 22 was 0.01 µg/L, the station is located upstream of Mt Meru.

In this case surface flowing water collects anthropogenic wastes from Arusha City elevating level of Pb in station number 21. Normally, emission from tire, brake wear, agrochemicals, municipal wastes and biomass burning are some of anthropogenic activities increasing level of Zn, Cu and Cr (Bem et al., 2003; Anderson et al., 2010). Mentioned sources of Zn and Cu are common anthropogenic activities conducted in the basin. In this phenomenon Zn, Cu and Pb have possibly been contributed by anthropogenic sources. High contribution of Al in the first component showed the influence of weathering in the level of metals. The first component represented high rate of weathering, health effect and anthropogenic activities. Therefore, close observation of dominant elements in the first component give message that level of metals in the basin was influenced by anthropogenic sources and geochemical processes.

Second component was dominated by DSi, Mn and Ni, second component showed the role of silicate weathering in influencing the level of metals in the basin. Concentration of DSi varies with different rocks; high level of DSi was measured on samples from Mt. Usambara whereas low level was measured from Mt. Kilimanjaro. Therefore, second factor relate the role played by metamorphic rocks.

WHO recommends daily uptake of less than 70 and 100 µg/L of Ni and Mn, respectively. These weight are higher than that of Pb in the first component suggesting health sensitivity of Mn and Ni are less than Pb.

Presence of Mn which was also high in the third factor explained the role played by redox reaction in the level of metals in the basin. Impact of rocks and weathering in the level of particulate trace elements was illustrated in table 6. High level of magnetic susceptibility (XLF) reflect the role played by rock whereas high level of TSM suggest role played by weathering in the level of particulate metals (Table 6).

Table 6. Factor analysis for particulate trace metals.

	1	2	3
V	0.948	-0.281	
Cu	0.939		0.294
Fe	0.934	-0.234	0.156
Pb	0.878	0.122	-0.433
Co	0.852	-0.401	0.125
Mn	0.782	-0.419	0.21
Zn	0.687	0.644	-0.226
Ni	0.686		-0.19
Cr	0.678	0.433	-0.531
Al	0.612	0.481	0.439
XLF	0.202	0.752	0.353
TSM	0.3	-0.543	-0.214
Eigenvalues	6.669	2.185	1.094
Contribution rate (%)	55.574	18.211	9.115
Accumulated contribution rate (%)	55.574	73.785	82.9

Therefore, overall message from factor analysis showed that level of metals in the basin was influenced by anthropogenic activities and natural sources. Impact of redox reaction and rate of weathering was also illustrated in influencing the level of metals in the basin.

5.3 Yield of trace elements from PRB to Indian Ocean

Flow of trace elements from upstream to river mouth was interrupted by various anthropogenic activities. Nyumba ya Mungu reservoir was one of anthropogenic feature influencing normal flow of materials from upstream to river mouth. Previous studies have shown that the reservoir was a sink of nutrients and organic carbon (Selemani et al., 2017a; Selemani et al., 2018). The estimate from this study has shown that in average 244.3, 0.01, 6.60, 0.03, 8.35, 42.70, 0.07, 0.33, 0.09, 0.04 kg of dissolved Al, Pb, V, Cr, Mn, Fe, Co, Ni, Cu, Zn sink into the reservoir per year. Similarly, 613×10^3, 0.18×10^3, 2.75×10^3, 0.29×10^3, 283×10^3, 364×10^3, 2.2×10^3, 0.7×10^3, 3.8×10^3 and 2.8×10^3 kg of particulate Al, Pb, V, Cr, Mn, Fe, Co, Ni, Cu and Zn sink in the reservoir per year. Biological uptake and settling are some of phenomenon reducing outflow of trace elements from the reservoir. Therefore, the reservoir also acted as a sink of trace elements suggesting that there was more input into the reservoir than outflow from the reservoir.

The river transported more Fe, Al and Mn to the coastal of Indian Ocean compared to other studied elements. The basin is dominated by volcanic rocks therefore presence of hematite minerals increased level of Fe. Presence of manganite is important source of Mn (Jun, & Martin, 2003). High level of Al downstream was contributed by Precambrian metamorphic rocks. In this case high flux of Al was due to weathering from Precambrian rocks downstream.

In average more than 99% of trace metal flowing to Indian Ocean were attached in particulate whereas dissolved trace metal flowing to Indian Ocean was less than 1%. Yield of trace metals in dissolved form from other tropical rivers including Sabaki and Gomati, showed that PRB had low yield compared to other tropical rivers (Table 4).

5.4 Water quality for human and aquatic ecosystem health

Most of the measured trace elements were below recommended drinking water standards with an exceptional of Al, Fe, V and Mn in some stations. As it was observed most of the content of Al, Fe, V and Mn came from rock weathering. Sampling was conducted in rainy season of which rainfall was one of the factors influencing rate of weathering. More researches are needed to test variability of trace elements in different season. High level of Al and Fe above recommended level was also observed in Nyamwamba River in Uganda, Rift valleys lakes and rivers in Ethiopia all are located in East Africa. According to authors Al and Fe in all rivers were contributed by geological features (Zinabu, & Pearce, 2003: Abraham, & Susan, 2017).

6. Conclusion

This study investigated concentration of trace elements in dissolved and particulate forms. Abundance of elements in most of the stations followed the following order Al>Fe>Mn> V> Ni>Cu> Zn> Cr>Pb which coincide to their order of abundance in the upper earth crust. The study revealed high spatial variation in which the concentration increased from upstream to river mouth. There was low level of trace elements in dissolved phase compared to that of particulate phase.

Bio-geochemical processes which control level of trace elements in the basin were redox reactions (Mn, Co and Ni), pH mediated reaction (V and Rb), temperature mediated reaction (V) and organic carbon complexation (V and Cu). Biological uptake and settling were observed in Nyumba ya Mungu reservoir which caused to decrease level of trace elements in the effluent water.

Concentration of Al, Fe, V and Mn in some stations was higher than recommended drinking water standards. Concentration of trace elements in dissolved phase varies with time, human influence and climatic condition. Therefore, this study recommends frequent monitoring on the level of trace element so as to understand the concentration and propose appropriate measures to be taken in order to prevent widespread of hazardous for the wellbeing of community and aquatic ecosystem health.

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Data availability statement

Experimental data has been made available under a Creative Commons Attribution 4.0License and is available for download from https://zenodo.org/deposit/4415161

References

Abraham, M.R., & Susan, T.B. (2017). Water contamination with heavy metals and trace elements from Kilembe copper mine and tailing sites in Western Uganda; implications for domestic water quality. *Chemosphere*, *169*, 281-287. https://doi.org/10.1016/j.chemosphere.2016.11.077

Ama., I.N., Nwajei, G. E., & Agbaire, N.P.O. (2017). Distribution of Trace Elements in Surface Water and Sediments from Warri River in Warri, Delta State of Nigeria. *World News of Natural Sciences, 11*, 65-82.

Anderson, L.D., Faul, K.L., & Paytan, A. (2010). Phosphorus associations in aerosols: What can they tell us about P bioavailability? *Marine Chemistry*, *120*(1-4), 44-56. https://DOI:10.1016/J.MARCHEM.2009.04.008

Bakyayita, G.K., Norrstrom, A.C., & Kulabako, R.N. (2019). Assessment of Levels, Speciation, and Toxicity of Trace MetalContaminants in Selected Shallow Groundwater Sources, Surface Runoff, Wastewater, and Surface Water from Designated Streams in Lake Victoria Basin, Uganda. *Hindawi, Journal of Environmental and Public Health, 2019*(2), 1-18. https://doi.org/10.1155/2019/6734017.

Bem, H., Gallorini, M., Rizzio, E., & Krzeminska M (2003). Comparative studies on the concentrations of some elements in the urban air particulate matter in Lodz City of Poland and in Milan, Italy. *Environment International*, *29* (4), 423-428. https://doi.org/10.1016/S0160-4120(02)00190-3

Buck, K.N., Lohan, M.C., Berger, C.J.M., & Bruland, K.W. (2007). Dissolved iron speciation in two distinct river plumes and an estuary: Implications for riverine iron supply. *Limnology Oceanography*, *52*(2), 843-855. https://doi.org/10.4319/lo.2007.52.2.0843

Chester, R., & Jickells, T.D. (2012). Marine Geochemistry, 3rd Edition. New Jersey, United States: Wiley-Blackwell.

Cosgrove, W.J., & Loucks, D. P. (2015). Water management: Current and future challenges and research directions. *Water resources research, 51*, 4823–4839. https://doi:10.1002/2014WR016869.

Elbaz-Poulichet, F., Seyler, P., Maurice-Bourgoin, L., Guyot, J., & Dupuy, C. (1999). Trace element geochemistry in the upper Amazon drainage basin (Bolivia). *Chemical Geology*, 157(3-4), 319-334.

Feng, C., Guo, X., Yin, S., Tian, C., Li, Y., & Shen, Z. (2017). Heavy metal partitioning of suspended particulate matter water and sediment water in the Yangtze Estuary. *Chemosphere*, 185, 717-725. https://doi.org/10.1016/S0009-2541(99)00015-7

Fernandes, A.M., Hissler, C., da Conceiç~ao, F. T., Junior, E. P. S., & Mortatti, J. (2016). Combined analysis of trace elements and isotopic composition of particulate organic matter in suspended sediment to assess their origin and flux in a tropical disturbed watershed. *Environmental Pollution*, *218*, 844-854. https://doi.org/10.1016/j.envpol.2016.08.008

Fu, J., Tang, X.L., Zhang, J., & Balzer, W. (2013). Estuarine modification of dissolved and particulate trace metals in major rivers of East-Hainan,China. *Continental Shelf Research*, *57*, 59-72. https://doi.org/10.1016/j.csr.2012.06.015

Fuller, C.C., & Harvey, J.R. (2000). Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona. *Environmental Science and Technology, 34* (7), 1150-1155. https://doi.org/10.1021/es990714d

GIBB, (1998). Updated Technical Appraisal Studies of the Mid-Western Towns Water Supply Project, Nairobi, Kenya, GIBB International.

Gurumurthy, G.P., Balakrishna, K., Tripti, M., Audry, S., Riotte, J., Braun, J.J., & Shanka, H.N.U. (2014). Geochemical behaviour of dissolved trace elements in a monsoon-dominated tropical river basin, Southwestern India. *Environmental Science and Pollution Research 21*(7), 5098-5120. https://doi.org/10.1007/s11356-013-2462-7

Hatje, V., Payne,T.E., Hill, D.M., McOrist,G., & Szymczak, R. (2003). Kinetic soft race element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading. *Environment International*, *29*(5), 619-629. https://doi: 10.1016/S0160-4120(03)00049-7.

Hu, B., Yang, Z., Wang, H., Sun, X., Bi, N., & Li, G. (2009). Sedimentation in the Three Gorges Dam and the future trend of Changjiang (Yangtze River) sediment flux to the sea. *Hydrology and Earth System Science, 13*(11), 2253-2264. https://DOI: 10.5194/hess-13-2253-2009

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary toxicology*, *7*(2), 60–72. https://doi.org/10.2478/intox-2014-0009

Javed, M., & Usmani, N. (2017). An Overview of the Adverse Effects of Heavy Metal Contamination on Fish Health. *Proceedings of the National Academy of Sciences, India Section B: Biological Sciences,* 89, 389–403. https://doi.org/10.1007/s40011-017-0875-7

Jickells, T., An, Z., Andersen, K.K., Baker, A., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I., & Torres, R. (2005). Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science, 308*(5718), 67-71. https://DOI: 10.1126/science.1105959

Jigyasu, D.K., Kuvar, R., Srivastava, N., Singh, S., Singh, I.B., & Singh, M. (2015). High mobility of aluminium in Gomati River Basin: implications to human health. *Current Science, 108* (3), 434-439. https://DOI:10.18520/CS/V108/I3/434-438

Jun, Y., & Martin ST (2003). Microscopic Observations of Reductive Manganite Dissolution under Oxic Conditions. *Environmental Science and Technology, 37* (11), 2363-2370. https://doi: 10.1021/es026254x.

Kihampa, H.H, De Wael, K., Lugwisha, E., & Van Grieken, R. (2013). Water quality assessment in the Pangani River basin, Tanzania: natural and anthropogenic influences on the concentrations of nutrients and inorganic ions. *International Journal of River Basin Management, 11*(1), 55-75. https://doi.org/10.1080/15715124.2012.759119

Kihampa, H.H., Potgieter-Vermaak, S., De Wael, K., Lugwisha, E., Van Espen, P., & Van Grieken, R. (2014) Concentration profiles of metal contaminants in fluvial sediments of a rural–urban drainage basin in Tanzania. *International Journal of Environmental Analytical Chemistry*, *94* (1), 77-98. https://DOI: 10.1080/03067319.2013.791976

Koukina, S., & Lobus, N. (2019). Major and Trace Element Distribution in Suspended Particulate Matter and Sediments of the Tropical River Estuary (South Vietnam) in H. I. Chaminé et al. (eds.), Advances in Sustainable and Environmental Hydrology, Hydrogeology, Hydrochemistry and Water Resources, Advances in Science, Technology & Innovation; Switzerland, Springer Nature. https://doi.org/10.1007/978-3-030-01572-5_16

Lu, S.G., Bai, S.Q., & Xue, Q.F. (2007). Magnetic properties as indicators of heavy metals pollution in urban top soils: a case study from the city of Luoyang, China. *Geophysical Journal International*, *171*(2), 568 - 580. https://DOI: 10.1111/j.1365-246X.2007.03545.x

Lydersen, E., Löfgren, S., & Arnesen, R.T. (2002). Metals in Scandinavian surface waters: effects of acidification, liming, and potential reacidification. *Critical Reviews in Environmental Science and Technology*, *32*(2-3), 73-295. https://DOI: 10.1080/10643380290813453

Ma, X., Zuo, H., Tian, M., Zhang, L., Meng, J., Zhou, X., Min, N., Chang, X., & Liu, Y. (2016). Assessment of trace elements contamination in sediments from three adjacent regions of the Yellow River using element chemical fractions and multivariate analysis techniques. *Chemosphere, 144*, 264-272. https://DOI: 10.1016/j.chemosphere.2015.08.026

Molander, C. (2015). Influence of excessive water on wastewater treatment performance, An analysis using key performance indicators; Master’s Thesis available at http://publications.lib.chalmers.se/records/fulltext/223718/223718.pdf accessed 27 October 2020.

Muiruri, J., Nyambaka, H., & Nawiri, M. (2013). Heavy metals in Water and Tilapia Fish from Athi-Galana-Sabaki Tributaries, Nairobi. *International Food Research Journal 20* (2), 891-896

Mzuza, M.K., Zhang, W., Kapute, F., & Selemani, J.R. (2017). Magnetic properties of sediments from the Pangani River Basin, Tanzania: Influence of lithology and particle size. *Journal of Applied Geophysics* 143, 42-49. https://DOI: 10.1016/j.jappgeo.2017.05.015

National Bureau of Statistics, (2013). Population distribution by age and sex. Available at http://ihi.eprints.org/2169/1/Age_Sex_Distribution.pdf [verified 25 September 2017]

Oelkers, E.H., Gislason, S.R., Eiriksdottir, E.S., Jones, M., Pearce, C.R., & Jeandel, C. (2011). The role of riverine particulate material on the global cycles of the elements. *Applied Geochemistry, 26*, S365-S369. https://doi.org/10.1016/j.apgeochem.2011.03.062

Onojake, M.C., Sikoki, F.D., & Akpiri, R.U. (2017). Surface water characteristics and trace metal level of the Bonny/New Calabar River estuary, Niger Delta, Nigeria. *Applied Water Science*, *7*, 945-959. https://doi.org/10.1007/s13201-015-0306-y

PBWB/IUCN, (2008). Basin Delineation Report. Pangani Basin Water Board, Moshi and IUCN Eastern and Southern Africa Regional Programme, Nairobi. Available https://cmsdata.iucn.org/downloads/ basin_delineation_report.pdf [verified 10 June 2017].

Reza, R., & Singh, G. (2010). Heavy metal contamination and its indexing approach for river water. *International Journal of Environmental Science and Technology*, 7, 785-792. https://doi.org/10.1007/BF03326187

Savenko, V.S. (2006). Principal features of the chemical composition of suspended load in World Rivers. *Doklady Earth Sciences*, *407*, 450–454. https://doi.org/10.1134/S1028334X06030238

Sayer, M.D.J., Reader, J.P., & Morris, R. (1989). The effect of calcium concentration on the toxicity of copper, lead and zinc to yolk-sac fry of brown trout, Salmo trutta L., in soft, acid water. *Journal of Fish Biology*, *35*(3), 323-332. https://doi.org/10.1111/j.1095-8649.1989.tb02985.x

Selemani, J.R., Zhang, J., Muzuka, A.N.N., Njau, K.N., Zhang, G., Maggid, A., Mzuza, M.K., Jin, J., & Pradhan, S. (2017b). Seasonal water chemistry variability in the Pangani River basin, Tanzania. *Environmental Science and Pollution Research International, 24*(33*)*,26092-26110. https://doi: 10.1007/s11356-017-0221-x.

Selemani, J.R., Zhang, J., Muzuka, A.N.N., Njau, K.N., Zhang, G., Mzuza, M.K., & Maggid, A. (2017a). Nutrients' distribution and their impact on PanganiRiver Basin's ecosystem – Tanzania. *Environmental Technology, 39*(6), 702-716. https://doi: 10.1080/09593330.2017.1310305.

Selemani, J.R., Zhang, J., Wu, Y., Muzuka, A.N.N., Njau, K.N., Zhang, G., Mzuza, M.K., Maggid, A., Zhang, M., & Qi, L. (2018). Distribution of organic carbon: possible causes and impacts in the Pangani River Basin ecosystem, Tanzania. *Environmental Chemistry, 15*(3), 137-149. https://doi.org/10.1071/EN17185

Shulkin, V., & Zhang, J. (2014). Trace metals in estuaries in the Russian Far East and China: Case studies from the Amur River and the Changjiang. *Science of the Total Environment, 499*, 196-211. https://doi: 10.1016/j.scitotenv.2014.08.015.

Strady, E., Dinh, Q.T., Nemery, J., Nguyen, T.N., Guedron, S., Nguyen, N.S., Denis, H., & Nguyen, P.D. (2017). Spatial variation and risk assessment of trace metals in water and sediment of the Mekong Delta. *Chemosphere, 179*, 367-378. https://doi: 10.1016/j.chemosphere.2017.03.105.

Tarvainen, T., Lahermo, P., & Mannio, J. (1997). Sources of trace metals in streams and headwater lakes in Finland. *Water, Air, and Soil Pollution, 94(1)*, 1-32. https://DOI:10.1023/A:1026465417921

Taylor, S.R., & McLennan, S.M. (1985). The geochemical evolution of the continental crust. *Reviews of Geophysics*, *33*(2), 241-265. https://doi.org/10.1029/95RG00262

TMA, (2015). Statement on the Status of Tanzania Climate 2015, available at http://www.meteo.go.tz/uploads/publications/sw1586355691-Statement%20%202015%20.pdf

Tosiani, T., Loubet, M., Viers, J., Valladon, M., Tapia, J., Marrero, S., Yanes, C., Ramirez, A., & Dupre, B. (2004). Major and trace elements in river-borne materials from the Cuyuni basin (southern Venezuela): evidence for organo-colloidal control on the dissolved load and element redistribution between the suspended and dissolved load. *Chemical Geology 211*, (3-4), 305-334. https://doi.org/10.1016/j.chemgeo.2004.07.001

Tripti, M., Gurumurthy, G.P., Balakrishna, K., & Chadaga, M.D. (2013). Dissolved trace element biogeochemistry of a tropical river, Southwestern India. *Environmental Science and Pollution Research, 20* (6), 4067-4077. https://doi.org/10.1007/s11356-012-1341-y

Tuna, A.L., Yilmaz, F., Demirak, A., & Ozdemir, N. (2007). Sources and distribution oftrace metals in the Saricay stream basin of southwestern Turkey. *Environmental Monitoring and Assessment, 125*(1-3), 47-57. https://DOI: 10.1007/s10661-006-9238-1

Walling, D. (2006). Human impact on land–ocean sediment transfer by the World's rivers. *Geomorphology, 79* (3-4), 192–216. https://doi.org/10.1016/j.geomorph.2006.06.019

Wang, H., Saito, Y., Zhang, Y., Bi, N., Sun, X., & Yang, Z. (2011). Recent changes of sediment flux to the western Pacific Ocean from major rivers in East and Southeast Asia. *Earth-Science Reviews, 108* (1-2), 80–100. https://doi.org/10.1016/j.earscirev.2011.06.003

Wang, S.L., Xu, X.R., Sun, Y.X., Liu, J.L., & Li, H.B. (2013). Heavy metal pollution in coastal areas of South China: a review. *Marine Pollution Bulletin 76* (1-2), 7-15. https://DOI: 10.1016/j.marpolbul.2013.08.025

WHO (2011). Guidelines for drinking-water quality. 4th edn. Switzerland. NC-SA 3.0 IGO. Available from: http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf [verified 2 January 2020].

Wu, Y., Zhang, J., Liu, S.M., Zhang, Z.F., Yao, Q.Z., Hong, G.H, & Cooper, L. (2007). Sources and distribution of carbon within the Yangtze River system. *Estuarine, Coastal and Shelf Science, 71*(1-2), 13-25. https://doi:10.1016/J.ECSS.2006.08.016

Wu, Y., Zhang, J., Ni, Z., Liu, S., Jiang, Z., & Huang, X. (2018). Atmospheric deposition of trace elements to Daya Bay, South China Sea:Fluxes and sources. *Marine Pollution Bulletin, 127,* 672-683. https://doi.org/10.1016/j.marpolbul.2017.12.046

Zhang, F., John, S.G., Zhang, J., Ren, J., Wu, Y., Zhu, Z., Liu, S., Zhu, X., Marsay, C.M., & Wenger, F. (2015). Transport and reaction of iron and iron stable isotopes in glacial meltwaters on Svalbard near Kongsfjorden: From rivers to estuary to ocean. *Earth and Planetary Science Letters* 424, 201-211. https://doi.org/10.1016/j.epsl.2015.05.031

Zinabu, G.M., & Pearce, N.J.G. (2003). Concentrations of heavy metals and related trace elements in some Ethiopian rift-valley lakes and their in-flows. *Hydrobiologia, 429* (1), 171-178. https:// DOI: 10.1023/A:1024856207478

Figure 1, Study map showing sampling stations and elevation, 22 stations were sampled from river mouth to the foot of Mt. Kilimanjaro (KLM) and Meru..

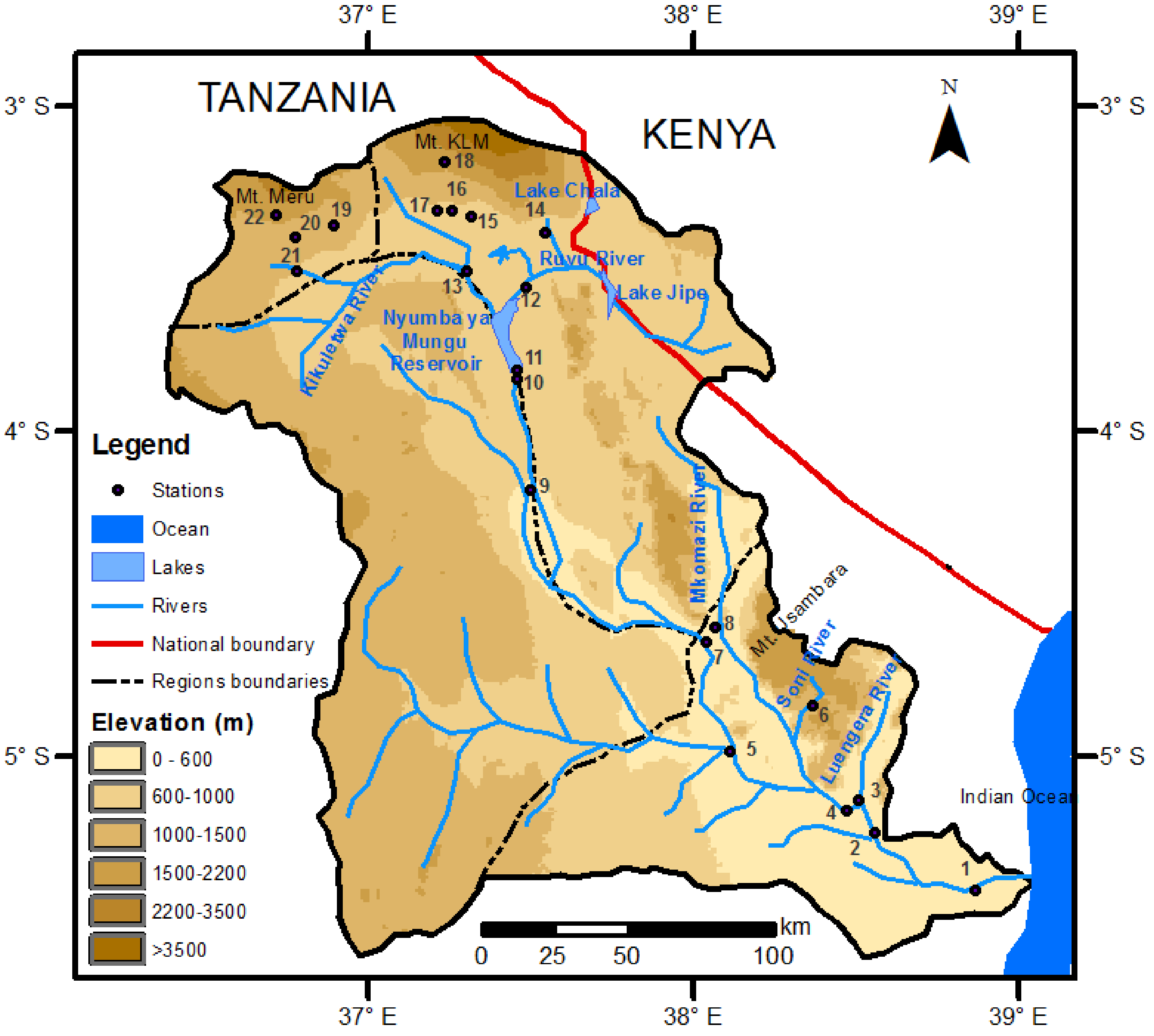

37° E
38° E
39° E
3° S
4° S
5° S
TANZANIA
KENYA
N
Mt. KLM
18
16
17
15
14
Mt. Meru
22
20
19
21
13
12
11
10
9
8
7
6
5
4
3
2
1
Lake Chala
Ruvu River
Lake Jipe
Nyumba ya Mungu Reservoir
Kikuletwa River
Mkomazi River
Mt. Usambara
Soni River
Luengera River
Indian Ocean
Legend
● Stations
Ocean
Lakes
Rivers
National boundary
Regions boundaries
Elevation (m)
0 - 600
600-1000
1000-1500
1500-2200
2200-3500
>3500
km
0
25
50
100

Figure 2, Level of dissolved elements from the reservoir (station 10) to river mouth (station 1), almost all elements decreased from reservoir to river mouth except Al..

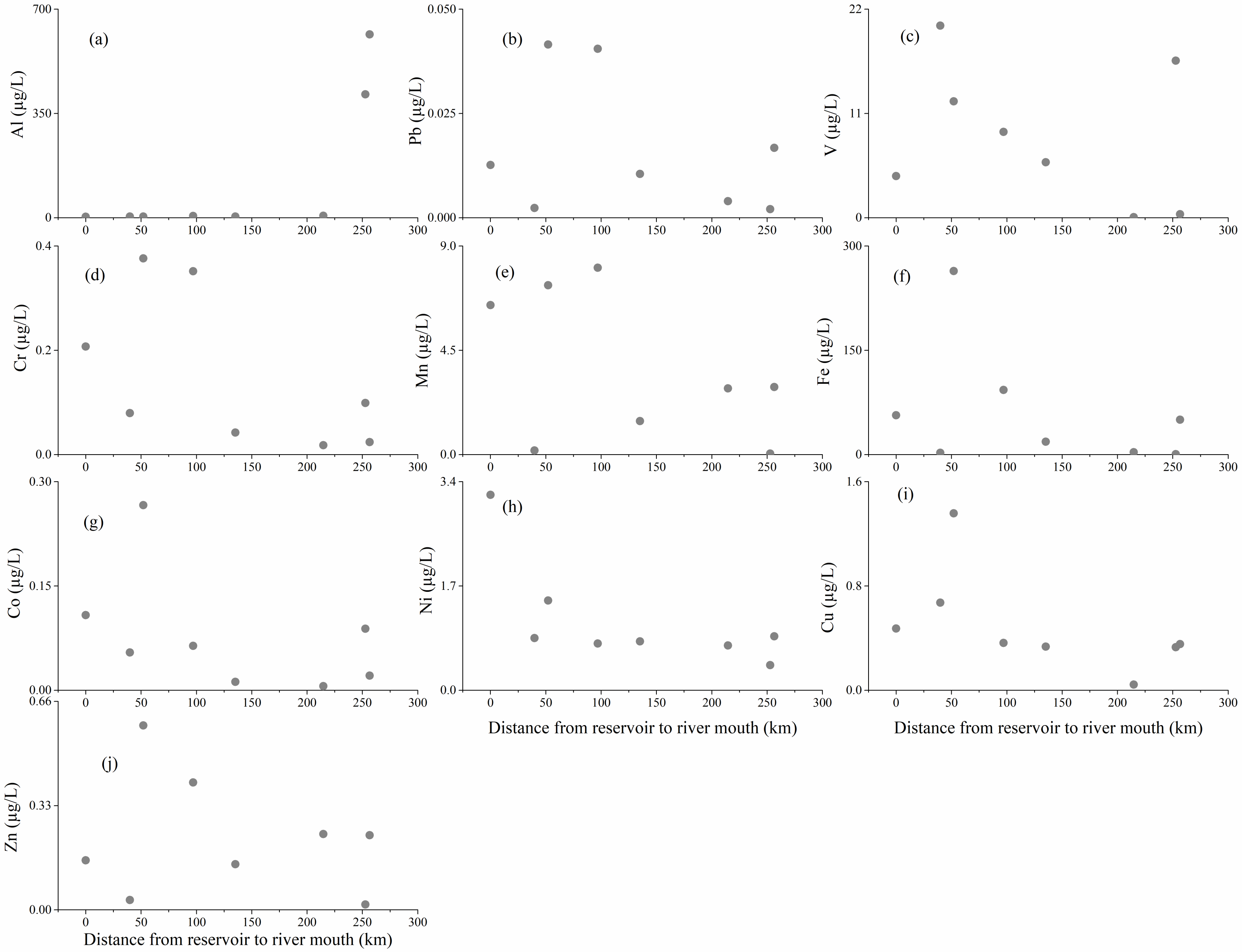

(a)
Al (µg/L)
700
350
0
(b)
Pb (µg/L)
0.050
0.025
0.000
(c)
V (µg/L)
22
11
0
(d)
Cr (µg/L)
0.4
0.2
0.0
(e)
Mn (µg/L)
9.0
4.5
0.0
(f)
Fe (µg/L)
300
150
0
(g)
Co (µg/L)
0.30
0.15
0.00
(h)
Ni (µg/L)
3.4
1.7
0.0
(i)
Cu (µg/L)
1.6
0.8
0.0
(j)
Zn (µg/L)
0.66
0.33
0.00
0
50
100
150
200
250
300
Distance from reservoir to river mouth (km)
Distance from reservoir to river mouth (km)
Distance from reservoir to river mouth (km)

Figure 3, Level of particulate elements from the reservoir (station 10) to river mouth (station 1), all elements increased from reservoir to river mouth..

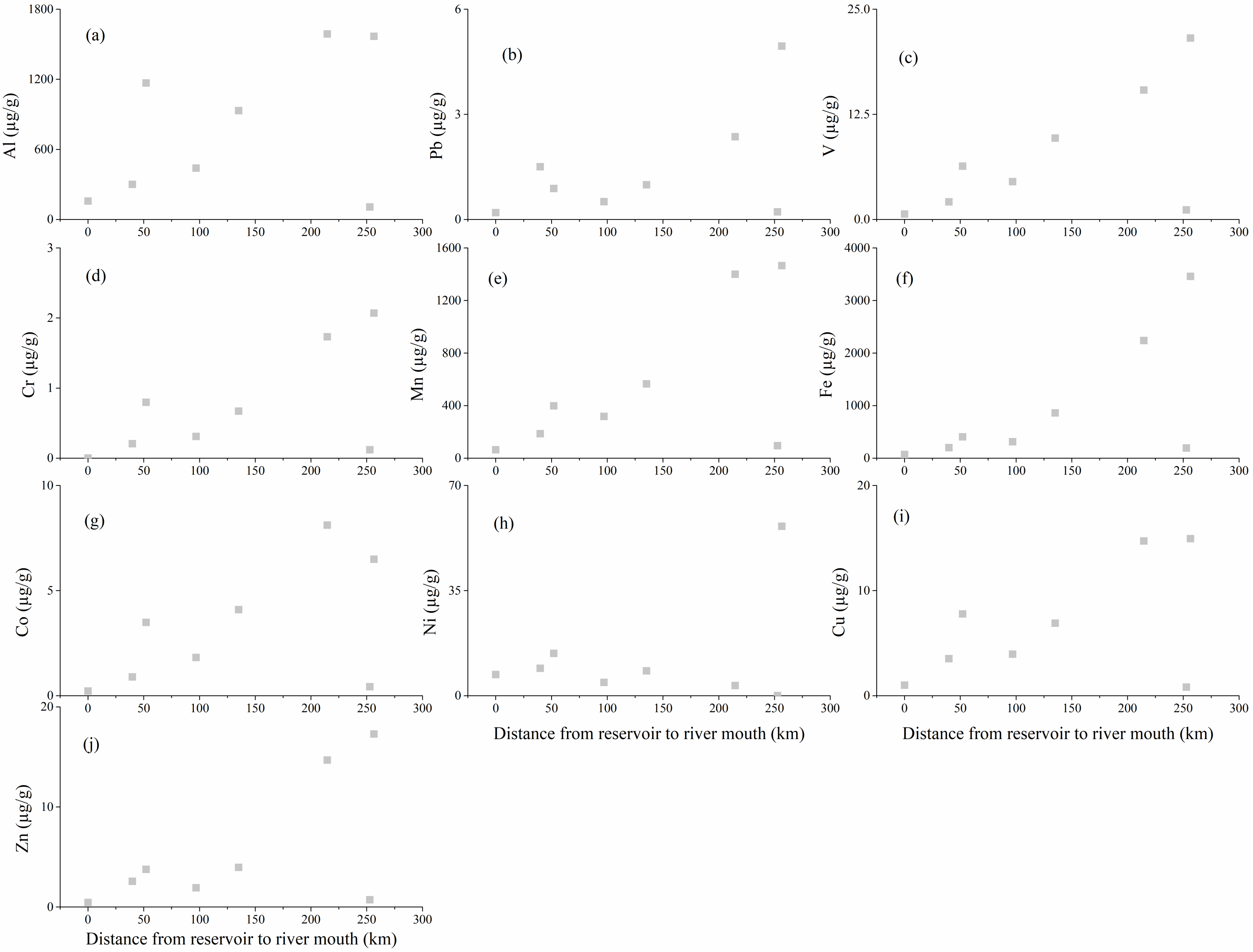

(a)
Al (μg/g)
0
600
1200
1800
(b)
Pb (μg/g)
0
3
6
(c)
V (μg/g)
0.0
12.5
25.0
(d)
Cr (μg/g)
0
1
2
3
(e)
Mn (μg/g)
0
400
800
1200
1600
(f)
Fe (μg/g)
0
1000
2000
3000
4000
(g)
Co (μg/g)
0
5
10
(h)
Ni (μg/g)
0
35
70
(i)
Cu (μg/g)
0
10
20
(j)
Zn (μg/g)
0
10
20
0
50
100
150
200
250
300
Distance from reservoir to river mouth (km)

Figure 4, Ratio of particulate/dissolved elements from low altitude to high altitude, the ratio decreased with the increasing altitude..

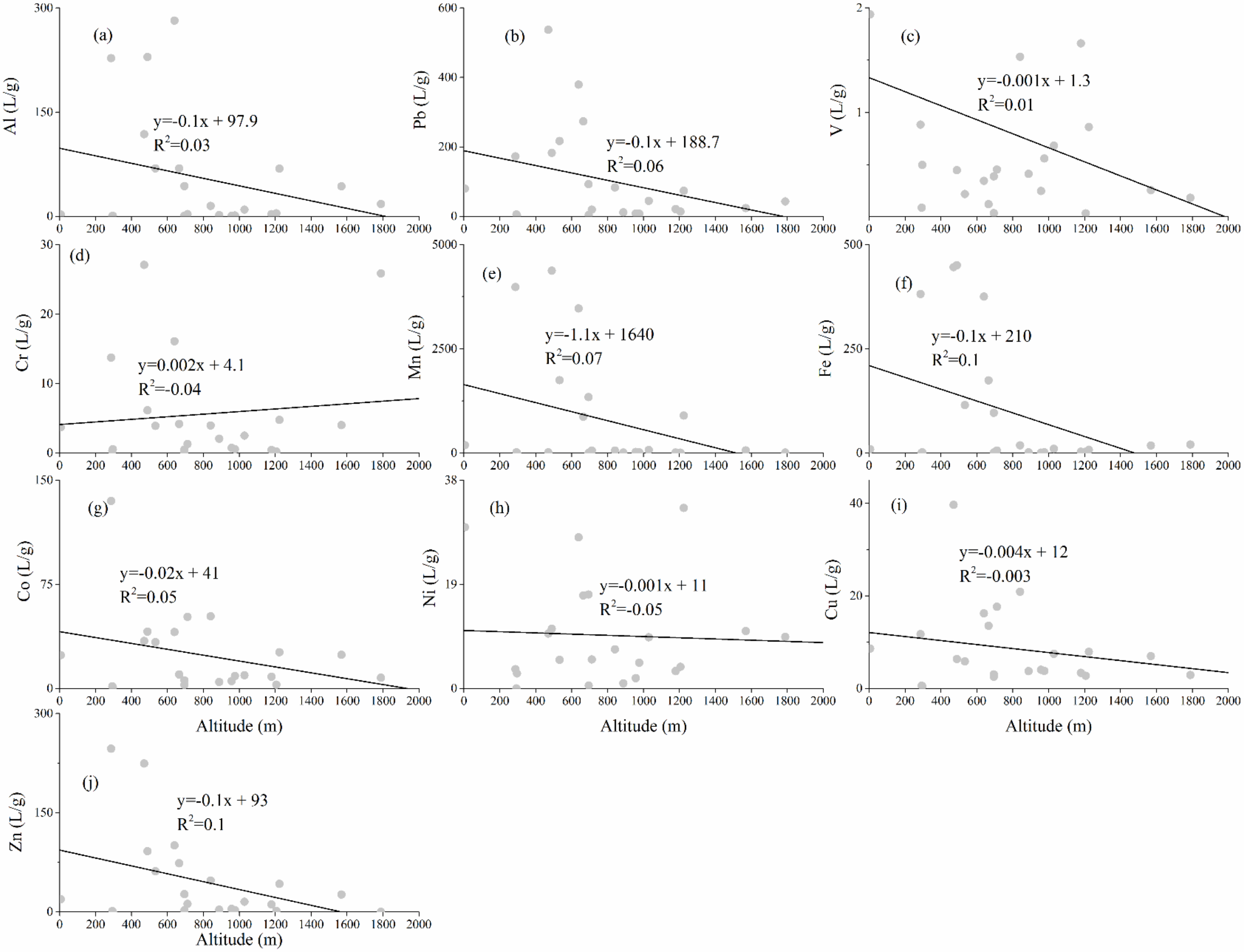

(a)
Al (L/g)
y=-0.1x + 97.9
R^2=0.03
(b)
Pb (L/g)
y=-0.1x + 188.7
R^2=0.06
(c)
V (L/g)
y=-0.001x + 1.3
R^2=0.01
(d)
Cr (L/g)
y=0.002x + 4.1
R^2=-0.04
(e)
Mn (L/g)
y=-1.1x + 1640
R^2=0.07
(f)
Fe (L/g)
y=-0.1x + 210
R^2=0.1
(g)
Co (L/g)
y=-0.02x + 41
R^2=0.05
(h)
Ni (L/g)
y=-0.001x + 11
R^2=-0.05
(i)
Cu (L/g)
y=-0.004x + 12
R^2=-0.003
(j)
Zn (L/g)
y=-0.1x + 93
R^2=0.1
Altitude (m)
0 200 400 600 800 1000 1200 1400 1600 1800 2000
0 150 300
0 200 400 600
1 2
0 10 20 30
0 2500 5000
0 250 500
0 75 150
0 19 38
0 20 40

Figure 5, Variation of ratio of particulate and dissolved trace metals against total suspended matter; the ratio increased with TSM..

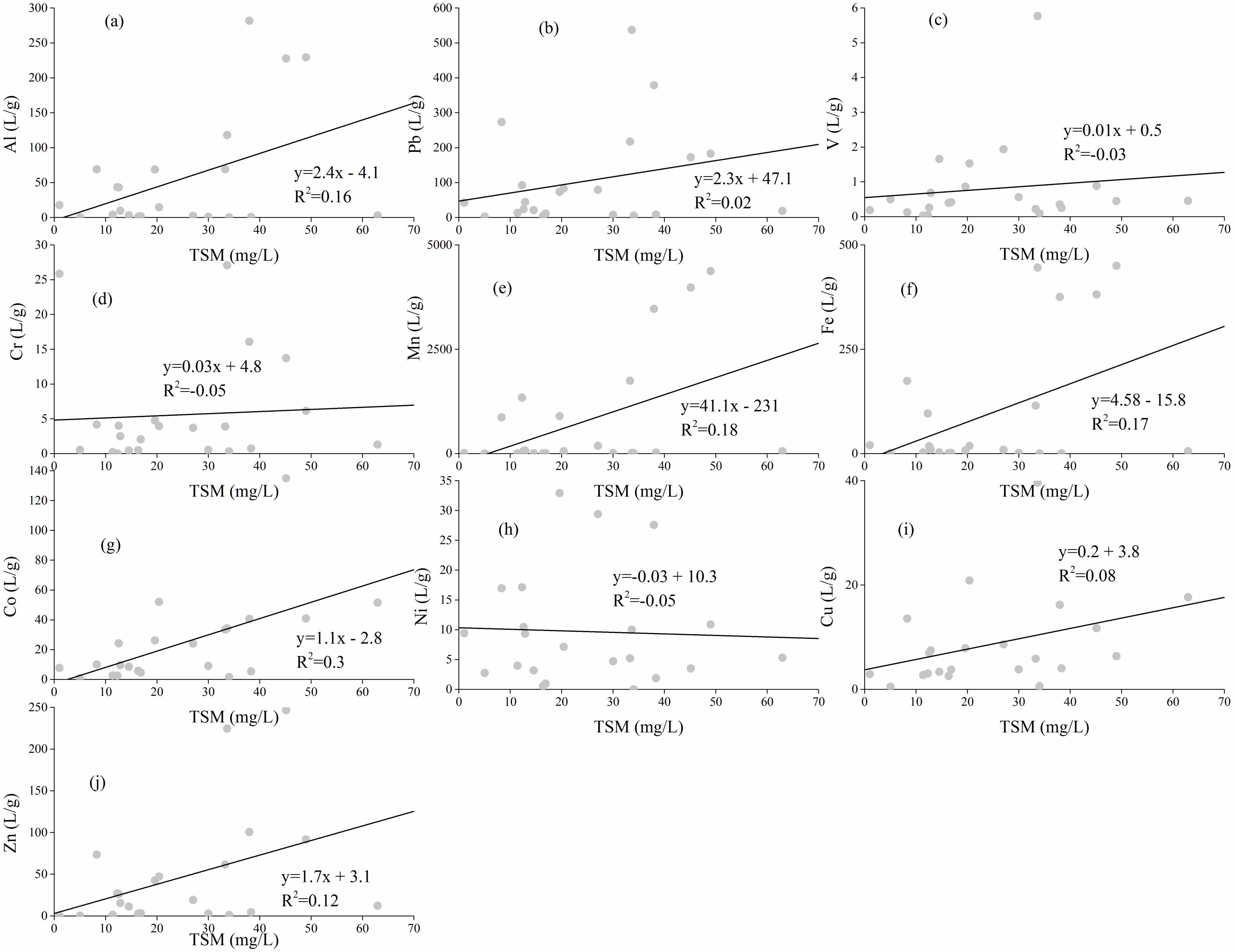
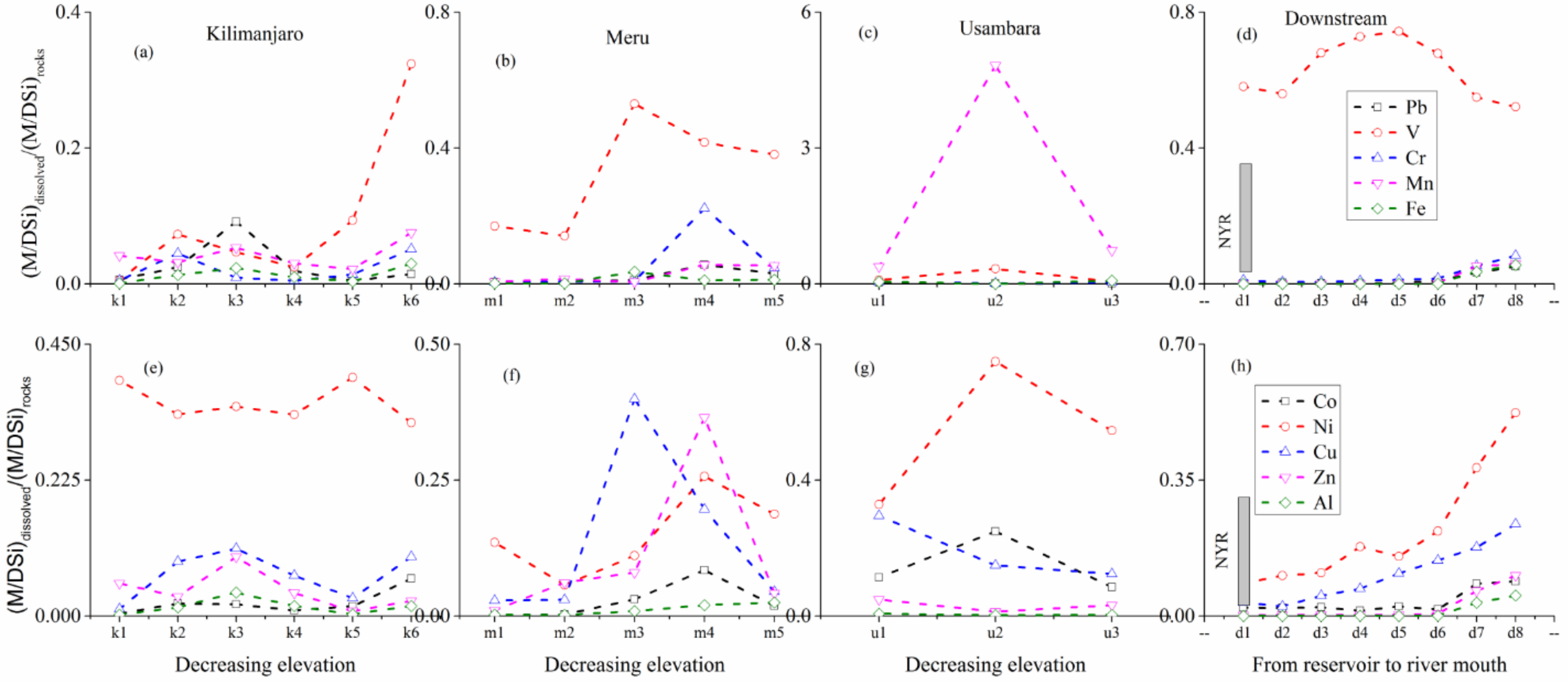

(a)
Al (L/g)
y=2.4x - 4.1
R2=0.16
TSM (mg/L)
(b)
Pb (L/g)
y=2.3x + 47.1
R2=0.02
TSM (mg/L)
(c)
V (L/g)
y=0.01x + 0.5
R2=-0.03
TSM (mg/L)
(d)
Cr (L/g)
y=0.03x + 4.8
R2=-0.05
TSM (mg/L)
(e)
Mn (L/g)
y=41.1x - 231
R2=0.18
TSM (mg/L)
(f)
Fe (L/g)
y=4.58 - 15.8
R2=0.17
TSM (mg/L)
(g)
Co (L/g)
y=1.1x - 2.8
R2=0.3
TSM (mg/L)
(h)
Ni (L/g)
y=-0.03 + 10.3
R2=-0.05
TSM (mg/L)
(i)
Cu (L/g)
y=0.2 + 3.8
R2=0.08
TSM (mg/L)
(j)
Zn (L/g)
y=1.7x + 3.1
R2=0.12
TSM (mg/L)
0
10
20
30
40
50
60
70

Figure 6, Weight of the dissolved metals to that of DSi and weight in the rocks. Figure shows stations on the slope of Mt. Kilimanjaro, Meru, Usambara and from Nyumba ya Mungu (NYR) to river mouth..


(M/DSi)$_{dissolved}$/(M/DSi)$_{rocks}$
(a)
Kilimanjaro
0.0
0.2
0.4
k1
k2
k3
k4
k5
k6
(b)
Meru
0.0
0.4
0.8
m1
m2
m3
m4
m5
(c)
Usambara
0
3
6
u1
u2
u3
(d)
Downstream
0.0
0.4
0.8
NYR
Pb
V
Cr
Mn
Fe
--
d1
d2
d3
d4
d5
d6
d7
d8
--
(M/DSi)$_{dissolved}$/(M/DSi)$_{rocks}$
(e)
0.000
0.225
0.450
k1
k2
k3
k4
k5
k6
(f)
0.00
0.25
0.50
m1
m2
m3
m4
m5
(g)
0.0
0.4
0.8
u1
u2
u3
(h)
0.00
0.35
0.70
NYR
Co
Ni
Cu
Zn
Al
--
d1
d2
d3
d4
d5
d6
d7
d8
--
Decreasing elevation
Decreasing elevation
Decreasing elevation
From reservoir to river mouth

Element	Pb	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Mean±SD	10.1±0.1	9.0±0.1	10.3±0.2	10.2±0.1	9.8±0.1	9.5±0.1	10.1±0.1	10.7±0.1	10.4±0.1	11.9±0.1
R^2 of standard line	0.999	0.999	1.0	0.999	1.0	0.999	1.0	0.999	1.0	0.999

River	Country	Pb	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	References
PRB (dissolved)	Tanzania	0.03±0.03 (0.01-0.1)	143±182 (3.6-616)	9.52±7.3 (0.05-21.5)	0.27±0.6 (0.02-2.6)	30.27±42 (0.05-490)	112.7±138 (0.7-395)	0.14±0.2 (0.01-0.58)	1.11±0.7 (0.32-3.19)	0.92±0.9 (0.04-3.86)	0.54±1.2 (0.02-5.56)	This study
Warri River	Nigeria	30			70	155	1050	30	30	30	190	Ama et al., 2017
Sabaki	Kenya	34			24	902.3			13.5		85.4	Muiruri et al., 2013
Bonny River	Nigeria	0.23			1.39		1.36	0.24	0.22	0.47	2.81	Onojake et al., 2017
Gomati River	India	4.3	5289	8.21	4.76	115	2080	2	7	7.34	16.9	Jigyasu et al., 2015
World averaged		0.08				34.7	66			1.45	0.61	Shulkin, & Zhang, 2014
				Leachable particulate and sediment metals								
PRB (particulate)	Tanzania	2.02±5 (0.13-24)	1855±3983 (15-9410)	7.86±12 (0.01-22)	1.82±6 (0.01-7)	839±1694 (20-7237)	1103±1585 (45-4464)	3.69±5.62 (0.03-20)	12.2±18 (0.02-23)	10.6±19 (0.12-33)	23.3±81 (0.04-86)	This study
PRB (Sediment)	Tanzania	21.5		148.5	72	1350		26.5	36.5	46	225	Hellar-Kihampa et al., 2014
Cay River	Vietnam	62.7	0.092	88.5	90.2	0.05	0.03	68.4	153	105	79.8	Koukina, & Lobus, 2019
Sorocaba River	Brazil				61			18	24	28	252	Fernandes et al., 2016
World averaged		25	0.09	120	85	0.001	0.05	19	50	45	130	Savenko, 2006

	Pb	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	DOC	Temp	pH	DSi	SO_4^{2-}	HCO_3^-	Ca	DO	XLF
Pb																			
Al	0.82**																		
V	-0.07	-0.05																	
Cr	0.73**	0.51*	0.20																
Mn	-0.12	-0.15	-0.18	-0.07															
Fe	0.38	0.63**	-0.13	0.22	-0.08														
Co	0.36	0.36	0.10	0.55**	0.69**	0.36													
Ni	0.28	0.37	-0.18	0.31	0.34	0.34	0.57**												
Cu	0.41	0.40	0.35	0.45*	-0.02	0.57**	0.41	0.11											
Zn	0.77**	0.48*	0.13	0.95**	-0.08	0.19	0.46*	0.18	0.53*										
DOC	-0.11	0.05	0.58**	0.01	0.26	0.35	0.40	-0.09	0.67**	-0.02									
Temp	-0.08	0.12	0.66**	0.05	0.17	0.24	0.41	0.12	0.13	-0.11	0.51*								
pH	0.05	0.05	0.60**	0.15	-0.19	-0.04	0.05	-0.33	0.34	0.14	0.44*	0.48*							
DSi	0.09	0.02	0.47*	0.32	-0.25	-0.11	0.02	0.32	0.17	0.28	0.05	0.10	0.25						
SO_4^{2-}	0.02	0.05	0.89**	0.32	-0.16	0.11	0.29	-0.13	0.42	0.21	0.64**	0.73**	0.58**	0.31					
HCO_3^-	-0.17	-0.13	0.90**	0.08	0.19	-0.08	0.34	-0.11	0.39	0.02	0.77**	0.73**	0.53*	0.29	0.86**				
Ca	0.05	0.01	0.12	0.25	0.89**	-0.02	0.87**	0.37	0.16	0.17	0.42	0.38	0.04	-0.07	0.23	0.44*			
DO	-0.02	-0.14	0.02	0.01	-0.46*	-0.37	-.49*	-0.5*	-0.08	0.08	-0.15	-0.38	0.30	0.10	-0.09	-0.19	-0.46*		
XLF	0.19	0.08	-0.03	0.37	-0.14	0.17	0.11	0.29	0.44*	0.45*	0.08	-0.36	0.05	0.65**	-0.05	-0.09	-0.06	0.12	

River name	Discharge (m^3/s)	Area (km^2)	Al	Pb	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
PRB (particulate)	15.1	43500	17.2 $x10^3$	54.2	236.1	22.7	16.0 $x10^3$	37.9 $x10^3$	71.1	617.7	163.6	189.3
PRB (dissolved)	15.1	43500	6.74	0.68$x10^{-3}$	0.12	6.11$x10^{-3}$	85.8$x10^{-3}$	4.33	2.96$x10^{-3}$	21.0$x10^{-3}$	19.0$x10^{-3}$	9.9$x10^{-3}$
Gomati (dissolved)	351.8	30,437	1928 $x10^3$	1.6 $x10^3$	2.9 $x10^3$	1.74 $x10^3$	41.9 $x10^3$	758.2 $x10^3$	0.73 $x10^3$	2.5 $x10^3$	2.7 $x10^3$	6.2 $x10^3$
Sabaki (dissolved)	72.6	69,900		1.11 $x10^3$		0.8 $x10^3$	22.4 $x10^3$			0.44 $x10^3$		2.8 $x10^3$

Factors	1	2	3
Cr	0.852	-0.154	
Pb	0.842		-0.396
Zn	0.831	-0.198	
Al	0.783		-0.399
Co	0.69	0.371	0.582
Cu	0.678	-0.399	0.27
DSi		0.736	-0.415
Mn		0.674	0.658
V	0.105	-0.659	0.45
Ni	0.483	0.587	0.149
Fe	0.59		-0.135
Eigenvalues	4.279	2.145	1.58
Contribution rate (%)	38.903	19.5	14.364
Accumulated contribution rate (%)	38.903	58.403	72.767

	1	2	3
V	0.948	-0.281	
Cu	0.939		0.294
Fe	0.934	-0.234	0.156
Pb	0.878	0.122	-0.433
Co	0.852	-0.401	0.125
Mn	0.782	-0.419	0.21
Zn	0.687	0.644	-0.226
Ni	0.686		-0.19
Cr	0.678	0.433	-0.531
Al	0.612	0.481	0.439
XLF	0.202	0.752	0.353
TSM	0.3	-0.543	-0.214
Eigenvalues	6.669	2.185	1.094
Contribution rate (%)	55.574	18.211	9.115
Accumulated contribution rate (%)	55.574	73.785	82.9