Tanzania Journal of Science 44(3): 136-151, 2018 ISSN 0856-1761, e-ISSN 2507-7961
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SPECIATION OF LEAD, CHROMIUM, CADMIUM, COPPER AND ZINC IN SEDIMENTS AND PLANTS ALONG MSIMBAZI RIVER IN DAR ES SALAAM, TANZANIA

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ABSTRACT

The speciation of lead, chromium, cadmium, copper and zinc in sediments and plants (pumpkin) along Msimbazi River in Dar es Salaam were determined using Atomic Absorption Spectrophotometry. Results in sediments indicated that the heavy metal contents (mg/kg) in the form of total trace metals ranged from 50.34 to 161.63 for Pb, 68.38 to 501.85 for Zn, 18.43 to 66.61 for Cu, 20.93 to 76.46 for Cr and BDL to 0.23 for Cd. The contents (mg/kg) in the form of metals bound to organic matter ranged from 18.24 to 46.58 for Pb, 27.64 to 228.62 for Zn, 3.55 to 16.76 for Cu, 1.37 to 4.10 for Cr whereas Cd was not detected. In plant samples results in forms of total labile heavy metals ranged from 0.86 to 1.46 for Pb, 2.68 to 4.59 for Zn, BDL to 0.41 for Cu and from not detected to 0.21 mg/kg for Cr. In the form of total heavy metals, the ranges were from 19.62 to 36.68 for Pb, 33.56 to 68.80 for Zn, 3.33 to 13.06 for Cu while Cr and Cd were not detected. It was generally found that the levels of lead in plant samples along Msimbazi River were above the permissible levels recommended by WHO and TBS.

Key words: Atomic Absorption Spectrophotometry, Metal speciation, heavy metals, trace metals and pollutants.

INTRODUCTION

Freshwater quality worldwide has remained one of the major problems of concerns due to a number of factors caused by human activities as a result of the rapid socio-economic growth (Thomas and Durham 2003). Rivers are valuable freshwater resources in different countries that not only provide habitats for nature conservation but also are used for recreation and various activities for economic growth (Benamer 2014). The existing freshwater bodies such as rivers are known to receive massive pollutants from different sources that include wastewater effluents from industries, agricultural activities and household activities (Msagati and Mamba 2011), which alter the quality of freshwater. Due to the effects of this pollution, the already limited water resource is rendered more unfit for both human and animal consumption, agricultural uses as well as failing to sustain the ecosystems (Savenije and Van-der-Zaag 2008). The sources of heavy metals in rivers include atmospheric deposition, domestic wastewater effluents, run-off from urban, industrial wastewater effluents and agricultural materials which are known to carry high concentrations of heavy metals (Nriagu and Pacyna 1988). Different ways of association of heavy metals with sediments and other matrices determine their availability and mobility. Thus, determination of heavy metal speciation in particular environmental matrices offers information on the reactions that govern their behaviour in such matrices and hence ease to determine the effect of the polluted

environmental and/or biological matrices (Ogunfowokan et al. 2013, Salomaons and Förstner 1980).

Msimbazi River in Tanzania flows through Dar es Salaam city and discharges its water into the Indian Ocean. Because of its location, the river has been turned into dumping site by different sectors and hence, it has been reported to be receiving significant loads of both treated and untreated wastewaters from industrial effluents, agricultural run-off and wash-off from the households (Bwathondi et al. 1991, Leonard et al. 2012). The river has been reported by different studies to contain high concentrations of heavy metals among other pollutants and thus its water quality has decreased to a level of being not safe for both agricultural and human uses (Ak'habuhaya and Lodenius 1988). In order to assess the actual public health impacts of the heavy metals in freshwater, the study of metal speciation is necessary due to the fact that toxicity of the metal differs from one species to another, that is, it is the specific species of the metal that determines the metal's mobility, bioavailability and potential toxicity to organisms (Tamunobereton-ari et al., 2011, Ashraf et al., 2012). The properties of just one species of an element may have such an adverse effect on living systems (even at extremely low levels) so that the total element concentration becomes of little value in determining the impact of the trace element (Sobczynski and Siepak 2001, Fagbote and Olanipekun 2010). Knowledge of trace metal speciation in water, sediments and plant is essential to understand their toxicity, accumulation, as well as the partitioning of elements between different phases as most of metals are adsorbed to colloidal particles or combined in complexes (Odobasic 2012). For instance, the inorganic forms of tin (Sn), and mercury (Hg) are much less toxic or even do not show toxic properties while the alkylated forms are highly toxic (Kapustova 2009, Sharma et al. 2009). On the contrary, inorganic forms of arsenic are poisonous, while the arsenic compounds present in fish and other seafood are actually harmless (Fulekar and Chhotu 2009, Okoro et al. 2012). Inorganic As(III) compounds are carcinogens while arsenobetaine is essentially non toxic. Cr(III) is considered to be an essential element while Cr(VI) is a carcinogen (Okoro et al. 2012). It is also known that inorganic tin compounds are essential for plants and some animals but tributyltin (TBT) is an endocrine disruptor (Akcay et al. 2003, Kihampa et al. 2011). Thus, the presence of toxic heavy metals in Msimbazi river, may adversely affect the health of the users of the water. The previous study on heavy metal speciation along Msimbazi River by Othman (Othman 2002) covered only water samples leaving out other matrices like sediments and plants which were covered in this study. This study therefore, reports on the speciation of lead, chromium, cadmium, copper and zinc in sediments and plants along Msimbazi River.
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MATERIALS AND METHODS

Study Area and Sampling Sites

The Msimbazi river that is about 35 km long flows across Dar es Salaam city from the higher areas of Kisarawe in the Coast region and discharges into the Indian Ocean (Kondoro 1977, EnviPro 2014).

The River has four major tributaries namely Sinza, Ubungo, Luhanga and Kinyerezi rivers.

The river and its tributaries flow through industrial, urban and agricultural areas where they pick heavy metals. In this study samples were collected from six sampling sites as shown in Figure 1. The sampling sites along Msimbazi river (i.e., Vingunguti, Matumbi, Tabata, Kigogo, Kajima and Magomeni Darajani named as A, B, C, D, E, and F, respectively) (Figure 1), were located

with the aid of a GPS device model Ricoh Caplio 500 SE.

Sample Collection and Treatment

Sediments and plant samples were obtained from the selected sites over a period of two months (between November 2013 and January 2014). All samples were collected in triplicate at each sampling location.

Sediment samples were collected from the site using clean plastic spoons and then mixed thoroughly. To avoid contamination, different clean sampling spoons were used to collect samples from each site. Each sample was kept in a precleaned plastic bag and labelled before transportation to the laboratory for investigation. From each site three such composite samples were collected.

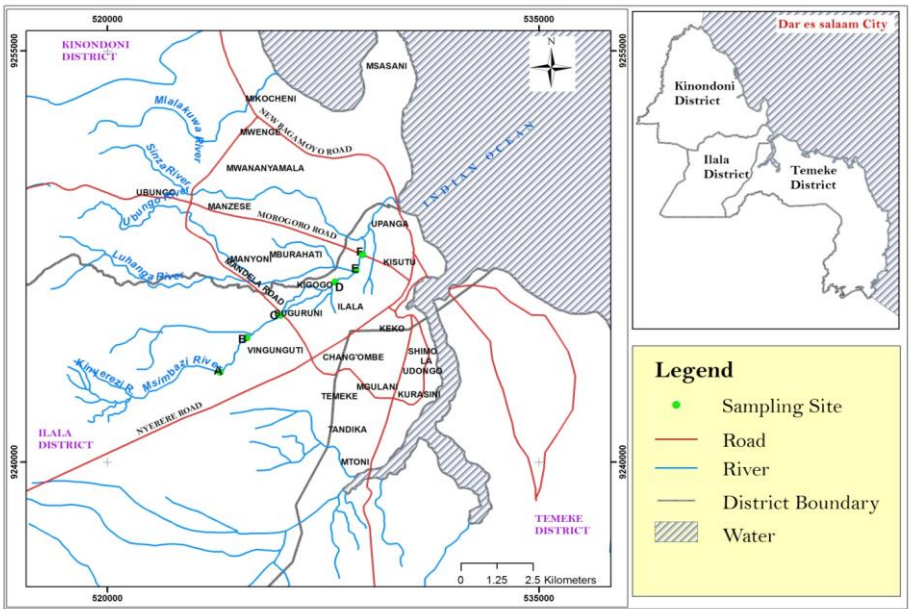


Figure 1: Sampling sites along Msimbazi river (GPS Laboratory, UDSM 2014). Where A = Vingunguti, B = Matumbi, C = Tabata, D = Kigogo, E = Kajima, F = Magomeni

Plant samples: Samples of pumpkin (Cucurbita maxima) were collected by uprooting fully grown plants, precleaned and stored in polythene bags and transported to the laboratory for preparation and analysis. Three such samples were collected from each site.

Analytical Method

The prepared samples were analyzed using atomic absorption spectrophotometry (AAS). Precision and accuracy was monitored with triplicate samples and blank samples. For calibration, synthetic standard solutions prepared in the corresponding media were used. The procedures were as reported elsewhere with some modification (Othman 2002, Benson et al., 2013, Kumar et al., 2014). Before analysis, calibration curves were prepared separately for each metal element ion by running different concentrations of standard solutions. Blank samples were analyzed and subtracted from the samples to correct for reagent impurities

and other sources of errors from the environment and the laboratory.

Speciation Analysis of Heavy Metals Sediment Samples

Total Trace Metal (TTM) species content in sediments were determined as reported elsewhere with some modification (Tokalioˇglu et al., 2000). About 2 g of the dried sediment sample were weighed and mineralized with a mixture of concentrated hydrofluoric acid and perchloric acid (1:5 HF:$HClO_4$), e.g., 2 mL: 10 mL, respectively for 1 hour. The resulting solution was then cooled and analyzed for total trace metal species content by FAAS. Field blanks, equipment blanks and a method blank were used. A method blank was made by mixing 1:5 HF acid and $HClO_4$ as explained previously. Exchangeable Trace Metal (ETM) species content in sediment was determined by taking 5.00 g of dried sediment sample, shaken for 10 minutes with 40 mL aqueous solution of 1 M magnesium chloride at pH 7.0 on a shaking device.

The pH was obtained by adding small amounts of 0.2 M HNO_3 acid dropwise to the solution whose pH was higher than 7. The resultant mixture was centrifuged for 30 minutes to separate solution and sediment. The supernatant was filtered and analyzed for content of exchangeable trace metals by FAAS. Bound to Organic Matter Trace Metal (BOMTM) species was determined by taking the residues from the determination of exchangeable trace metals and added 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 solution, which was adjusted to pH 2 with 0.02 M HNO_3 acid, and the mixture was heated to 85 ± 2 °C for 2 hours with occasional agitation. Then a 3 mL aliquot of 30% H_2O_2 was applied for 2 hours before a 15 mL portion of 20% H_2O_2 (pH 2 using 0.2 M HNO_3 acid) were added. The sample was again heated to 85 ± 2 °C for 2 hours. After cooling, 25 mL of 3.2 M ammonium acetate in 20% (v/v) HNO_3 were added and the sample was diluted to 50 mL. The solution was agitated continuously at room temperature for 30 minutes to prevent back-sorption of extracted metals onto the oxidized sediments. Separation of solution and sediment was accomplished by centrifuging for 30 minutes. The supernatant was analyzed by AAS to give content of Bound to Organic Matter Trace Metal (BOMTM) species whereas the residue was washed twice with distilled water and used in the next step i.e. the determination of residual trace metal species content. Field blanks, equipment blanks and a method blank were used. A method blank was made by carrying out the complete sample analytical procedure to all reagents (0.02 M HNO_3 acid, 30% H_2O_2 solution adjusted to pH 2, 20% H_2O_2 solution with pH 2 adjusted using 0.2 M HNO_3 acid, 3.2 M NH_4OAc solution and 20% v/v HNO_3 acid) were used in the volume of 25 mL and 50 mL, respectively. Residual Trace Metal (RTM) species were determined by using the residue from the determination of exchangeable trace metals step which was dried and mineralized with a mixture of concentrated hydrofluoric acid and perchloric acid (5:1) in a teflon beaker. The digestion was at first performed with a solution of concentrated perchloric acid (2 mL) and hydrofluoric acid (10 mL) in a teflon beaker and the solution evaporated almost to dryness by heating. Subsequently a second addition of perchloric acid (1 mL) and hydrofluoric acid (10 mL) was made and again the mixture was evaporated to near dryness. Finally concentrated perchloric acid alone was added and the solution evaporated slowly until white fumes were obtained. The residue was dissolved in 10 mL of 3 M hydrochloric acid and diluted to

25 mL using deionized water. The resulting solution was then analyzed for total trace metal (TTM) content by AAS. This gave the residual trace metal content of the sample (Odobasic 2012, Mrutu et al. 2013). Field blanks, equipment blanks and a method blank were used. A method blank was prepared by carrying out the complete sample analytical procedure to all reagents (concentrated HF acid and $HClO_4$ acid and 3 M HCl acid) used in the volume of 2 mL, 10 mL and 10 mL, respectively as used in the sample processing (Solomon et al.,, 2016, Kumar et al., 2014, Benson et al., 2013).

Plant (Pumpkin Leaves) Samples:

Plant sample infusions were prepared by allowing 5.00 g of the sample to infuse with 500 mL of deionized water at 95 °C for 15 minutes. The extract was filtered using Whatman filter paper No 41 and acidified with 10 mL of 2 M nitric acid and the amounts of the elements in the solution determined by FAAS. This gave the concentration of Soluble Trace Metal (STM) species in the plant samples. Field, equipment and method blanks were used. A method blank was prepared by adding HNO_3 acid (10 mL, 2 M) into deionized water (500 mL). A 1 g plant sample was weighed and placed into a conical flask. The sample was then digested with a mixture of 16 mL of pure concentrated HNO_3 acid and 4 mL of pure concentrated $HClO_4$ acid. The mixture was heated for 60 minutes until no more brown fumes were evolved and the solution began to give off white fumes. After cooling the digest was quantitatively transferred to a 50 mL volumetric flask and diluted to volume with 2 M nitric acid. This solution was then analyzed using FAAS to obtain the concentration of Total Trace Metal (TTM) species in the plant sample (Hester and Harrison 2000). Field blanks, equipment blanks and a method blank were used. A method blank used was prepared by carrying out the complete sample analytical procedure to all reagents (pure concentrated HNO_3 acid, pure concentrated $HClO_4$ acid and 2 M HNO_3 acid) used in the same volume as used in the sample processing above (Kihampa and Wenaty 2013).

RESULTS AND DISCUSSION

Results of different forms of speciation for the five selected heavy metals in this study are presented in various Tables and Figures in this section. Table 1, presents the permissible levels of the five studied heavy metals in portable water as set by WHO and other regulatory Authorities ((USEPA 2012, WHO 2007, EPA 2009 and EU 2014).

Table 1: Standard permissible levels (Total Concentrations) of the studied heavy metals in potable water (mg/L).

Standard Organization	Cd	Cr	Cu	Pb	Zn
WHO (2011)	0.003	0.05	2.0	0.01	5.0
USEPA (2012)	0.005	0.1	1.3	0.02	-
EPA (2009)	0.01	0.1	1.3	0.02	5.0
EU (2014)	0.005	0.05	2.0	0.01	-

Concentrations of Heavy Metal Species in Sediment Samples

The concentrations determined for triplicate samples were computed into average values and standard deviation (SD) as presented in Table 2.

Table 2: Average Concentrations (mg/kg) of Total Trace Metal (TTM) Species in Sediments

Heavy Metals	Concentrations of Heavy Metal Species in Sediments				Concentrations of Heavy Metal Species in Plant (Pumpkin Leaves)	
	Total Trace Metal (TTM)	Exchangeable Trace Metal (ETM)	Bound to Organic Matter Trace Metal (BOMTM)	Residual Trace Metal (RTM)	Soluble Trace Metal (STM)	Total Trace Metal (TTM)
			Sampling Site A (Vingunguti)			
Cu	24.13 ± 6.10	0.39 ± 0.15	6.47 ± 0.20	10.12 ± 2.1	0.38 ± 0.03	3.33 ± 0.76
Cr	20.93 ± 3.80	1.02 ± 0.01	1.37 ± 0.15	19.03 ± 1.50	0.21 ± 0.02	< 0.1
Cd	< 0.0125	< 0.005	< 0.005	< 0.005	< 0.005	< 0.025
Pb	161.63 ± 3.80	5.28 ± 1.52	26.40 ± 5.13	50.93 ± 2.50	1.26 ± 0.04	19.62 ± 1.26
Zn	68.38 ± 2.53	3.83 ± 1.50	27.64 ± 0.20	21.69 ± 1.50	4.59 ± 0.25	40.36 ± 1.26
			Sampling Site B (Matumbi)			
Cu	66.61 ± 5.86	0.46 ± 0.21	16.76 ± 1.50	67.47 ± 2.00	0.01 ± 0.002	4.12 ± 0.76
Cr	30.60 ± 3.08	0.32 ± 0.02	4.10 ± 0.10	27.19 ± 1.70	< 0.02	< 0.1
Cd	< 0.0125	< 0.005	< 0.005	0.09 ± 0.00	< 0.005	< 0.025
Pb	115.67 ± 6.32	5.34 ± 1.50	46.58 ± 2.50	53.80 ± 3.50	1.46 ± 0.06	30.67 ± 1.30
Zn	501.85 ± 3.80	4.37 ± 2.13	217.98 ± 1.50	204.14 ± 2.50	4.10 ± 0.35	39.90 ± 7.60
			Sampling Site C (Tabata)			
Cu	23.30 ± 5.12	0.15 ± 0.02	9.40 ± 1.10	24.09 ± 2.50	0.37 ± 0.02	7.80 ± 1.26
Cr	34.07 ± 3.80	0.27 ± 0.02	3.11 ± 0.15	49.46 ± 2.50	< 0.02	< 0.1
Cd	< 0.0125	< 0.005	< 0.005	< 0.005	< 0.005	< 0.025
Pb	51.48± 3.81	5.04 ± 1.50	32.07 ± 1.50	17.51 ± 1.50	1.02 ± 0.05	20.68 ± 1.04
Zn	288.01 ± 4.12	4.05 ± 1.51	228.61 ± 1.70	124.05 ± 3.50	4.12 ± 0.5	33.56 ± 1.00
			Sampling Site D (Kigogo)			
Cu	18.43 ±	0.29 ±	8.50 ±	9.98 ±	0.41 ±	12.78 ±

	3.80	0.10	1.60	1.50	0.15	1.26
Cr	76.46 ± 14.38	0.19 ± 0.03	2.31 ± 0.20	66.12 ± 1.90	< 0.02	< 0.1
Cd	< 0.0125	< 0.005	< 0.005	< 0.005	< 0.005	< 0.025
Pb	50.34 ± 3.80	7.95 ± 1.50	18.24 ± 1.00	9.65 ± 1.50	0.97 ± 0.07	36.68 ± 0.76
Zn	136.80 ± 3.54	3.30 ± 2.12	71.49 ± 2.50	51.93 ± 2.00	3.62 ± 0.25	56.38 ± 1.13
Sampling Site E (Kajima)						
Cu	30.58 ± 5.01	0.22 ± 0.02	3.55 ± 0.95	26.78 ± 5.25	< 0.01	6.01 ± 0.76
Cr	60.27 ± 9.61	0.25 ± 0.04	2.27 ± 0.10	53.66 ± 3.50	< 0.02	< 0.1
Cd	0.24 ± 0.006	< 0.005	< 0.005	< 0.005	< 0.005	< 0.025
Pb	60.07 ± 3.83	5.72 ± 2.10	24.94 ± 4.00	28.22 ± 3.10	0.86 ± 0.15	27.95 ± 0.63
Zn	158.65 ± 3.81	3.34 ± 1.54	46.99 ± 4.00	82.14 ± 3.00	2.68 ± 0.30	68.80 ± 1.26
Sampling Site F (Magomeni)						
Cu	43.15 ± 3.82	BDL	6.33 ± 1.80	34.03 ± 4.50	0.12 ± 0.04	13.06 ± 1.76
Cr	66.08 ± 14.46	0.21 ± 0.02	2.57 ± 0.17	86.44 ± 5.50	< 0.02	< 0.1
Cd	0.17 ± 0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.025
Pb	73.10 ± 3.85	5.79 ± 1.61	23.63 ± 5.54	21.07 ± 4.50	2.76 ± 0.17	34.25 ± 1.76
Zn	337.26 ± 5.13	2.72 ± 0.50	186.43 ± 5.00	123.92 ± 4.50	5.20 ± 0.45	41.59 ± 1.40

The results presented in Table 2 indicate that lead and zinc exist in river sediments predominantly as total trace metal (TTM) with the highest mean concentration of lead being 161.63 ± 3.8 mg/kg (Figure 2) at sampling site A (Vingunguti) and zinc having high concentration of 68.38 ± 2.53 at location B (Matumbi). Vingunguti site is located within the urban area with different industries including food processing industries, Vingunguti abattoir and leachate from old Vingunguti dump site that might have contributed to the observed elevated concentration of TTM species of lead. However, the total concentrations of Pb at all locations were below the maximum permissible limit (200 mg/kg) set by TBS (TBS 2008) for sediments. Thus, the variations of the concentrations of total trace metal (TTM) of lead between the sampling sites may be attributed to different levels of chemicals in the effluents discharged from industries and other human activities (i.e., automobile garages and car wash) taking place within the vicinity of the respective sampling sites. Figure 2 presents the observed variations of different chemical species of lead in sediments.

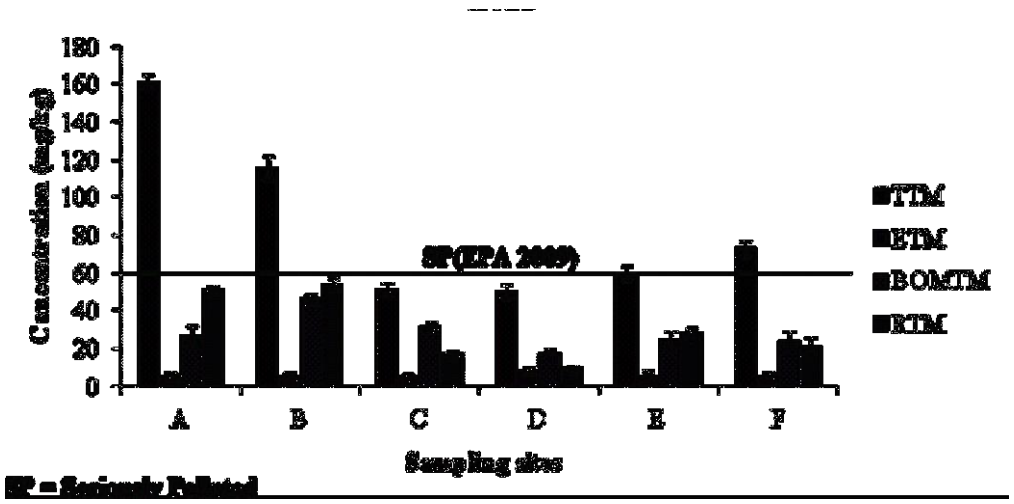


Figure 2: Concentration of Different Speciation Forms of Lead in the Sediment Samples, where, A = Vingunguti, B = Matumbi, C = Tabata, D = Kigogo, E = Kajima, F = Magomeni

The obtained lead species were observed to vary significantly in the sediment samples between sampling sites as shown in Figure 2 and confirmed by the analysis of variance (ANOVA) ($P < 0.0001$). Generally, the amount of lead occurred in large amount in the form of TTM (56.89%) as it was pointed out earlier. The lower concentration of lead was found in the form of RTM (20.1%) and BOMTM (19.1%) whereas the least amount was in the form of ETM (3.9%). The trend of association of lead in the sediments was then observed to be in the order: total trace metals (TTM) > residual trace metals (RTM) > bound on organic matter trace metals (BOMTM) > exchangeable trace metals (ETM). The concentrations for all forms ranged from 5.04 to 161.63 mg/kg. Generally the concentrations of all species of lead in sediments were observed to decrease from sampling site A (Vingunguti) to sampling site F (Magomeni) as indicated in Figure 3.

The observed trend in Figure 3, indicates the availability of lead sources (direct input from the sources) at the vicinity of sampling sites A and B, and that as moving away from these sites along the river heavy metal concentrations decreases. This trend is attributed to the effect of factors like dilution due to the increase in water volume caused by additional water from different streams that join the river. The trend also suggest that different anthropogenic activities are concentrated near sites A and B that might have been contributing to the elevated levels of lead species at sites, together with existing chemistry of sediment-water interface and the metal species can explain the diminishing behaviour of lead species along the river. It was also noted that the mean concentrations of lead were relatively higher than those reported by Othman (2001) for Msimbazi River sediment, Mwegoha and Kihampa (2010) for Msimbazi River, Mrutu et al. (2013) for Msimbazi River but were lower than those reported by Bungala (2002) for Mzinga River in Dar es Salaam, Tanzania (Table 3).

Copper was visually observed to be dominated by TTM and RTM with higher concentration at sampling site B (Matumbi). The concentration 67.47mg/kg was the highest at location B in the form of Residual Trace Metal (RTM) (Figure 4). The contribution of copper speciation forms TTM, RTM, BOMTM and ETM were 47.8%, 40%, 11.8% and 0.4%, respectively.

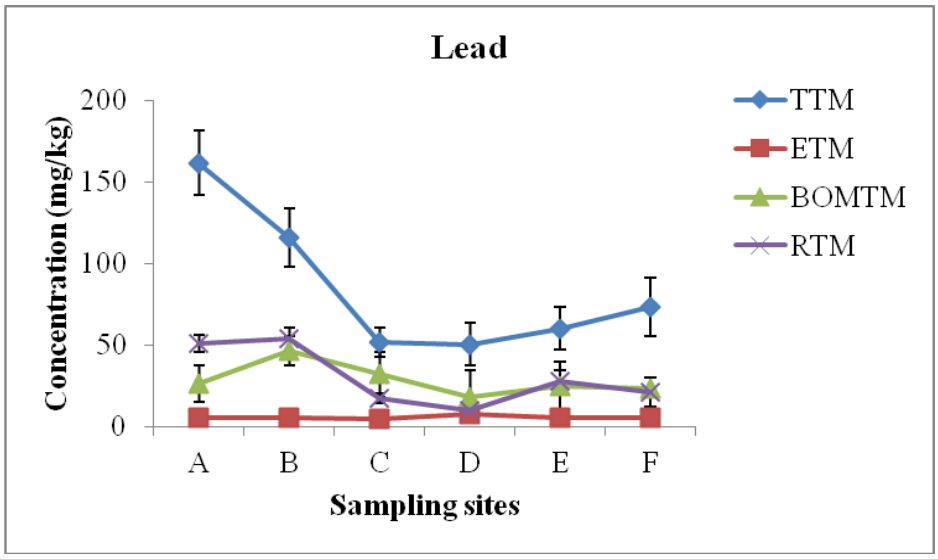


Figure 3: Variation of Concentrations of different speciation forms in along Msimbazi River.

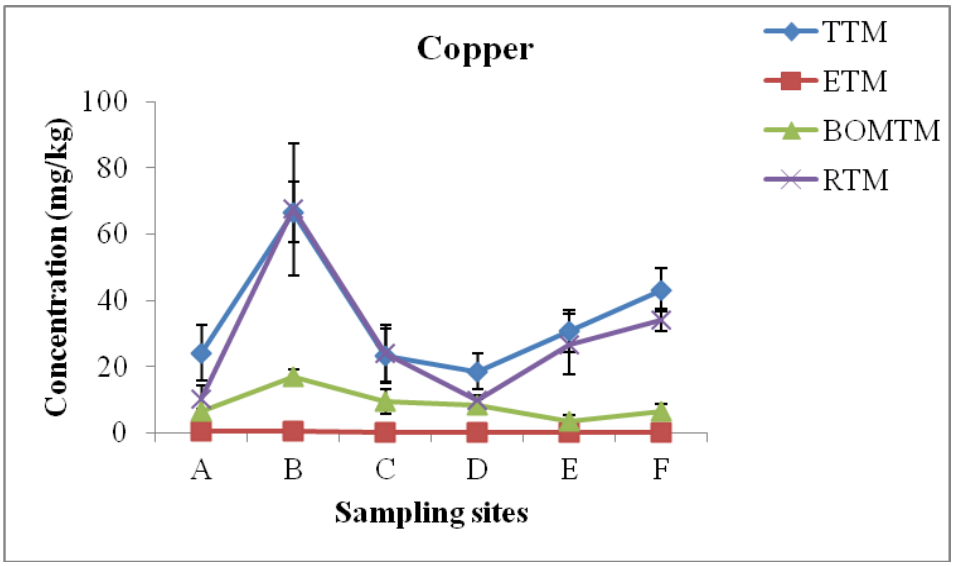


Figure 4: Variation of Concentrations of different speciation forms in along Msimbazi River

For chromium, the highest observed mean concentration of 86.44 ± 5.5 mg/kg was found to be in the form of residual trace metal (RTM) at Magomeni sampling location (Figure 5). This sampling site located within densely populated and industrialized area. It should also be noted that Msimbazi River and particularly at this sampling site receives effluents that are laden with different chemicals from different industries located in the vicinity of Msimbazi River basin including textile industries whose effluents are known to contain chromium (Mwegoha and Kihampa 2010).

Table 3: Levels of Heavy Metals (mg/kg) in Sediments at Rivers Msimbazi and Mzinga

Metals	This Study	Masimbazi River, Othman (2001)	Mzinga River, Bungala (2002)	Msimbazi River, Mwegoha & Kihampa (2010)	Msimbazi River, Mrutu et al., 2013	Mzinga River, Mtanga & Machiwa (2007)
Pb	85.38	49.2	1110.75	13.663	56.4	14.6
Cu	34.37	27.7	710.25	13.908	Bdl	Bdl
Cd	0.068	1.7	62.0	0.342	2.7	1.05
Cr	45.07	26.2	1202.25	348.935	50.5	22.7
Zn	248.49	161.6	13606.25	Bdl	120.0	35.5

Chromium originates from metal alloys, pigments for paints, cement, paper and rubber materials. The high concentration of chromium in sediments observed at location F (Magomeni) (Figure 5) can also be attributed to the waste inputs contributed by Luhanga stream which pours its water in Msimbazi River. Sampling location F is at the area of the river which receives pollutant contributions from almost all the streams that join Msimbazi River and has led to high levels of heavy metal pollution. However, the total concentrations of chromium at all locations were below the maximum permissible limits set by TBS for sediments (TBS 2008). The percentages of distribution of speciation forms of chromium in all the sampling sites were RTM (51.1%), TTM (45.8%), BOMTM (2.7%) and ETM (0.4%). The highest level of chromium (76.46 mg/kg) in the form of Total Trace Metal (TTM) species was found at location D (Kigogo) (Figure 5). The mean concentrations for all forms of chromium ranged between 1.015 and 76.46 mg/kg. The highest level of chromium reported was higher than that reported by Othman (2001) in Msimbazi River sediment but lower than those reported by Bungala (2002) for Mzinga River in Dar es Salaam, Tanzania, Mrutu et al. (2013) for Msimbazi river and Mwegoha and Kihampa (2010).

For cadmium, most sampling locations were found to have concentration of cadmium species below detection limit (BDL). The highest level of cadmium (0.24 mg/kg) was found at location E (Kajima) in the form of Total Trace Metal (TTM) species, and was found to exist in TTM (82%) and RTM (18%) speciation forms only.

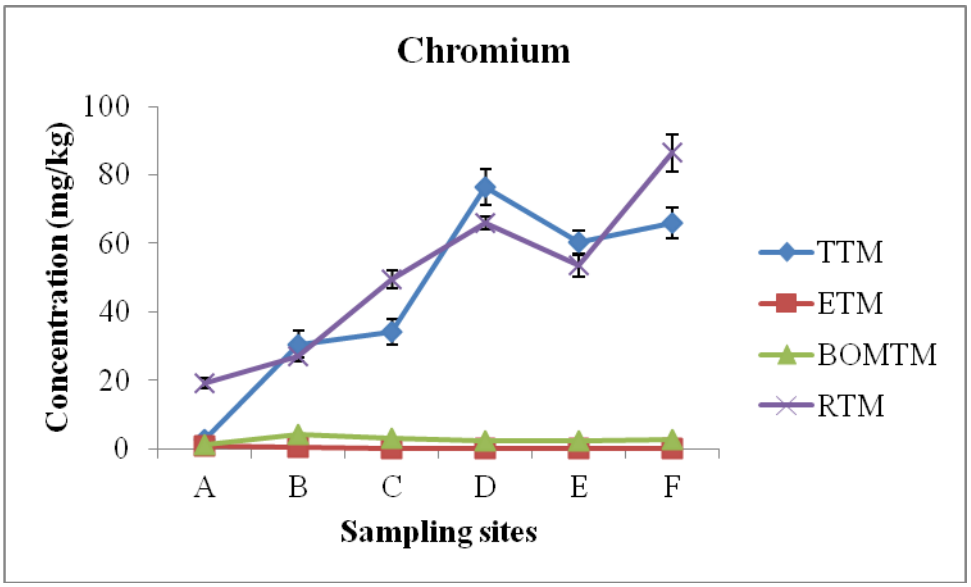


Figure 5: Concentration of Different Speciation Forms of Chromium in Sediment Samples; A = Vingunguti, B = Matumbi, C = Tabata, D = Kigogo, E = Kajima, F = Magomeni

Concentrations of Heavy Metal Species in Plant (Pumpkin Leaves) Samples

Lead was found in pumpkin leaves to exist predominantly in the form of total trace metal (TTM) (95.3%). The highest mean concentration of total trace metal was 36.68 ± 0.76 mg/kg (Figure 6), recorded at sampling station D (Kigogo) which is densely populated with many petrol stations and car-washes. The elevated lead concentration observed at location D may be explained by the number of anthropogenic activities in the vicinity of this location such as polluted stream from Kigogo garage which discharge effluents comprising oil into the river as well as the contribution of other pollutants from Luhanga stream. Furthermore, near sampling location D there is a lot of wastes dumped in the river that might lead to the addition of different chemicals like heavy metals into the river and hence be transferred to the pumpkin plants in the course of irrigation using the polluted river water. One-way ANOVA revealed the significant difference in the mean values among the sampling stations and the two forms ($P < 0.0001$). The concentrations of lead at all locations in TTM form exceeded the maximum permissible levels set by WHO (WHO 2011). The range in the content of heavy metals in mg/kg of dried vegetables was 19.62 to 36.68. The highest concentration was hundred times higher than the maximum concentration limits set. The concentrations of lead in the form of STM (4.7%) ranged from 0.86 to 2.76 mg/kg which according to the WHO (2011) and TBS (2008) were above the maximum concentration limits set. The mean concentrations of lead were higher than those reported by Othman (2001), Kihampa et al. (2011) and Mubofu (2012) but lower than those reported by Bungala (2002) (Table 4).

Table 4: Levels of heavy metals (mg/kg) in pumpkin leaves at Msimbazi River, Mzinga River and other places.

Metals	This study	Msimbazi River Othman (2001)	Mzinga River Bungala (2002)	Closed Dumpsite Kihampa et al., (2011)	Kariakoo Market Mubofu (2012)
Pb	26.64	4.24	48.25	11.29	0.059
Cu	7.85	9.53	291.5	14.32	0.0016
Cd	< 0.025	0.23	24.75	1.04	0.004
Cr	< 0.1	4.14	32	5.51	Bdl
Zn	46.77	44.54	591.5	47.67	0.0034

Bdl = Below detection limit.

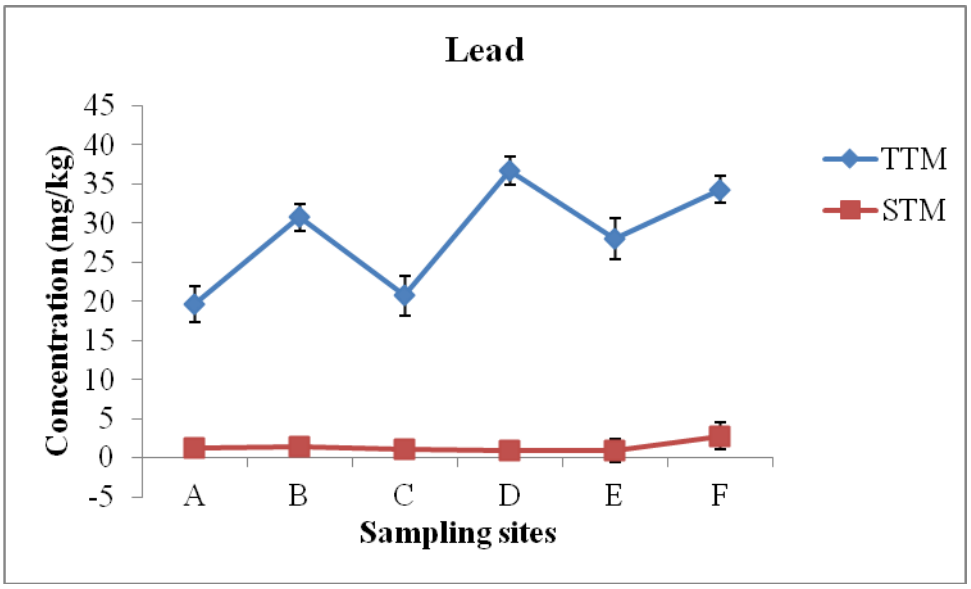


Figure 6: Concentration of Different Speciation Forms of Lead in Cucurbita maxima Samples. A = Vingunguti, B = Matumbi, C = Tabata, D = Kigogo, E = Kajima, F = Magomeni

The concentrations of chromium and cadmium speciation forms in pumpkin leaves from all sampling locations were below the detection limits. The amount of wastes dumped into Msimbazi River is large such that sometimes cause the river water in some areas to trickle along during dry season and thus leading to the increase of heavy metal concentrations. It has generally to be noted that the presence of high levels of heavy metals (lead, zinc, cadmium, copper and chromium) in Msimbazi River is mainly caused by effluents from industries, car wash sites and fuel tanker-flushing activities taking place at Kigogo Bridge as well as agricultural practices involving the use of fertilizers and pesticides taking place in upstream areas.

The total concentrations of zinc at all locations except at Kajima sampling location were below the maximum permissible level (60 mg/kg) for vegetables (Kihampa et al, 2011). The amounts of zinc were found to predominate in the form of TTM (92%) and were scarce in the form of STM (8%). It is only at sampling location E (Kajima) where the level of zinc (68.8 mg/kg) exceeded the permissible levels set by both WHO (2011) and TBS (2008) in the TTM speciation form. The levels of zinc in TTM speciation form ranged from 33.56 to 68.8 mg/kg of dried vegetables while in the STM speciation form ranged from 2.68 to 5.20 mg/kg. The mean concentration of zinc was higher than those reported by Othman (2001) and Mubofu (2012) but lower than those reported by Bungala (2002) and Kihampa *et al*., (2011). In all samples analyzed, the amount of copper occurred largely in the form of TTM (97.3%) and less in the form of STM (2.7%). In the TTM speciation form the concentration of copper ranged from 3.33 to 13.06 mg/kg and ranged from < 0.01 to 0.41 mg/kg for STM speciation form.

Generally the elevated levels of lead that were observed in the sediments and plants of Msimbazi River are due to the inflowing streams from Vingunguti areas that consists of different chemical wastes from industrial and domestic effluents as well as automobile garages and car wash that discharge into Msimbazi River (Mwegoha and Kihampa, 2010). Other human activities which can cause elevation of the levels of lead in the environment include combustion of leaded fuels; lead smelting and refining, brass manufacture, production of storage batteries, production of anti-knock compounds of lead alkyl in the form of tetraethyllead and tetramethyllead, production of leaded paints, agricultural application of lead arsenate (Mtanga and Machiwa 2007, WHO 2007, Mwegoha and Kihampa 2010, Mrutu et al. 2013). The high levels of lead at different sites in this study are of great concern as lead has been recognized for centuries as a cumulative general metabolic poison. Although the total concentrations of chromium at all locations in sediments and plants were below the maximum permissible limits set by both WHO (2011) and TBS (2008) its availability poses risk to human health. Once chromium is ingested by organisms it may result into health complications. Exposure to chromium may result into respiratory toxicity, kidney complications, septum atrophy, immune reactions, damage to circulatory and nerve tissues. Chromium originates from metal alloys, pigments for paints, and cement, paper and rubber materials as one of the components (EPA 2009, Ogunfowokan et al. 2013, Guertin 2004).

CONCLUSIONS

The concentrations and speciation of the heavy metals; lead, chromium, cadmium, copper and zinc were studied in samples of sediment and pumpkin leaves from Msimbazi River. Two speciation forms of heavy metals in plant samples and four speciation forms of heavy metals in sediment samples were determined with the aid of the speciation scheme. The trend of lead and copper speciation in sediments was: TTM > RTM > BOMTM > ETM with higher concentrations observed at sampling sites A (Vingunguti,) and B (Matumbi) for lead and sampling site B for copper. For pumpkin leaves samples, the concentrations of lead were found to be above the WHO and TBS Maximum Concentration Limits (MCLs) set in all sampling stations and its speciation followed the trend; TTM > STM. Chromium and cadmium were not detected in any form in plant samples from all the sampling stations. For sediment samples, the highest level of chromium was found at Kigogo in the form of TTM. Investigations on the mitigation measures on the high levels of heavy metals along Msimbazi

River should be thought and implemented. Industries located along this river should treat properly their wastewaters before discharging into the environment.

ACKNOWLEGEMENTS

Authors are thankful to the Chemistry Department of the University of Dar es Salaam, Tanzania for providing research facilities.

REFERENCES

Ak'habuhaya J, Lodenius M 1988 Metal pollution of river Msimbazi, Tanzania. *Environ. Int.* **14**: 511-514.

Akcay H, Oguz A, Karapire C 2003 Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Res.* **37**: 813 - 822.

Ashraf MA, Maah MJ, Yusoff I, Ghararibreza M 2012 Speciation of heavy metals in the surface waters of a former tin mining catchment, Chemical Speciation and Bioavailability, 24: doi:10.3184/095422912X13259575370081

Benamer MA 2014 Chemical Speciation and Spatial Distribution of Heavy Metals and Their Adsorption onto Sediments of The Berg River, South Africa. PhD Thesis, University of Cape Town, South Africa

Benson NU., Anake WU., Olanrewaju IO 2013 Analytical Relevance of Trace Metal Speciation in Environmental and Biophysicochemical Systems; *Am. J. Anal. Chem.* **4**:633 – 641

Bungala AOS 2002 *Concentration and physico-chemical forms of heavy metal pollutants in Yombo, Mzinga and Kizinga rivers in Dar es Salaam, Tanzania*. MSc Thesis, Chemistry Department, University of Dar es Salaam.

Bwathondi POJ, Nkotagu HH, Mkuula S 1991 Pollution of the Msimbazi valley. Report commissioned by National Environmental Management Council (NEMC), Dar es Salaam, Tanzania.

EPA 2009 National primary drinking water regulations. Environmental Protection Agency Washington, DC.

EU 2014 (Drinking water) regulations. European Union Commission. Statutory instruments SI No 122

EnviPro 2014 Projection completion report: Restoration of the Msimbazi river. Environmental Professionals Organization, Dar es Salaam, Tanzania

Fagbote EO, Olanipekun EO 2010 Speciation of heavy metals in sediment of Agbabu bitumen deposit area, Nigeria. *J. Appl. Sci. Environ. Manage*. **14**: 47 - 51.

Fulekar MH, Chhotu DJ 2009 Phytoremediation of heavy metals: Recent techniques. *Afr J Biotech*. **8**: 921-928.

Guertin J 2004 Toxicity and Health Effects of Chromium (All Oxidation States); Chapter 6, CRC Press LLC, p-213.

Kapustova S 2009 Heavy metals in the mountains streams. *Oecological Montana* **18**: 27 - 30.

Kihampa C, Mwegoha JSW, Shemdoe RS 2011 Heavy metals concentrations in vegetables grown in the vicinity of the closed dumpsite. *Int. J. Environ. Sci*. **2**: 889 - 895.

Kihampa C, Wenaty A 2013 Impact of mining and farming activities on water and sediment quality of the Mara river basin, Tanzania. *Res. J. Chem. Sci*. **3**: 15-24.

Kondoro JWA 1977 Dispersion of Heavy Metals along Msimbazi Basin in Dar es Salaam, Tanzania, *Tanz. J. Sci*. **23**: 1 - 10.

Kumar R, Rani M, Gupta H, Gupta B 2014 Trace Metal fractionation in water and sediments of an urban river stretch. *Chem. Spec. Bioavail.* **26**: 199 - 209

Leonard LS, Mwegoha WJS, Kihampa C 2012 Heavy metal pollution and urban

agriculture in Msimbazi river valley: Health risk and public awareness. *Int. J. Plant. Anim. Environ. Sci*. **2**: 107-118.

Mrutu A, Nkotagu HH, Luilo GB 2013 Spatial distribution of heavy metals in Msimbazi River mangrove sediments in Dar es Salaam coastal zone, Tanzania. *Int. J. Environ. Sci.* **3**: 1641-1655.

Msagati TAM, Mamba BB 2011 Development of supported liquid membrane techniques for the monitoring of trace levels of organic pollutants in wastewaters and water purification systems. *J. Phys. Chem. Earth* **36**: 1167-1177.

Mtanga A, Machiwa J 2007 Assessment of heavy metal pollution in sediment and polychaete worms from Mzinga Creek and Ras Dege mangrove ecosystems, Dar es Salaam, Tanzania. *Western India Ocean J. Mar. Sci*. **6**: 125-135.

Mubofu 2012 Heavy metal content in some commonly consumed vegetables from Kariakoo market, Dar es Salaam, Tanzania. *Tanz J Sci*. **38**: 201-207.

Mwegoha WJ, Kihampa C 2010 Heavy metal contamination in agricultural soils and water in Dar es Salaam City, Tanzania. *Afr. J. Environ. Sci. Technol*. **4**: 763-769.

Nriagu JO, Pacyna JM 1988 Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **333**: 134-139.

Odobasic A 2012 Determination and speciation of trace heavy metals in natural water by DPASV in water quality monitoring and assessment. Voudouris (Ed) InTech, Croatia. 429 - 456.

Ogunfowokan AO, Oyekunle JA, Olutona GO, Atoyebi AO, Lawa A 2013 Speciation study of heavy metals in water and sediments from Asunle river of the Obafemi Awolowo University, Ile-Ife, Nigeria. *Int. J. Environ. Prot.* **3**: 6-16.

Okoro HK, Fatoki OS, Adekola FA 2012 A review of sequential extraction procedures for heavy metal speciation in soil and sediments. 1(181), OMICS publishing.

Othman OC 2001 Heavy metals in green vegetables and soils from vegetable gardens in Dar es Salaam, Tanzania. *Tanz. J. Sci*. **27**: 37-48.

Othman OC 2002 Speciation of Cadmium, Copper, Lead and Zinc in the Waters of River Msimbazi Dar es Salaam, Tanzania. *Tanz. J. Sci.* **28**: 25-35.

Salomaons W, Förstner U 1980 Trace metal analysis of polluted sediments. Part 2. Evaluation of environmental impact. *Environ. Technol. Lett*. **1**: 506 - 517

Savenije HHG, Van-der-Zaag P 2008 Integrated water resources management: concepts and issues. *J. Phys. Chem. Earth* **33**: 290-297.

Sharma RK, Agrawal M, Marshall FM 2009 Heavy metals in vegetables collected from production and market sites of a tropical urban area of India. *J. Food Chem. Toxicol. **47***: 583 - 591.

Sobczynski T, Siepak J 2001 Speciation of heavy metals in bottom sediments of lakes in the area of Wielkopolski National Park. *Pol. J. Environ. Stud*. **10**: 463 - 474.

Solomon A, Rasheed K, Olanipekun E 2016 Spatial Distribution and Speciation of Heavy Metals in Sediment of River Ilaje, Nigeria, *RJPAC, **10**: 1-10.*

Tamunobereton-ari I., Omubo-Pepple VB., Tamunobereton-ari NA 2011 Speciation of heavy metals (Cu, Pb, Ni) pollutants and the vulnerability of groundwater resource in Okrika of Rivers State, Nigeria, *Am. J. Sci. Ind. Res*. **2**: 69-77

TBS 2008 Potable/Drinking water - specifications, 2nd Ed. TZS 789: 2008. Tanzania Bureau of Standards. 26-27.

Thomas J, Durham B 2003 Integrated water resource management: looking at the whole picture. *Desalination* **156**: 21–28.

Tokalio˘glu S, ¸ Kartal S, Elçi L 2000 Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure, *Anal. Chim. Acta* **413**: 33–40.

USEPA 2012 Edition of the drinking water standards and health advisories. US Environmental Protection Agency Washington, DC.

WHO 2007 Health Risks of Heavy Metals from long-range transboundary air pollution. World Health Organization: Copenhagen. 5-113.

WHO 2011 Guidelines for Drinking-Water Quality, Fourth edition World Health Organization, Geneva. 180-365.