Levels of Arsenic and other environmentally significant elements in Upper Pote River, Mashonaland East Province, Zimbabwe: Impact on riverbank garden vegetables irrigated using water from the river

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ABSTRACT

The aims of the present study were (a) to assess the impact of the Runhanga Cattle Dip in Zimbabwe, historically based on arsenic dip, on the levels of arsenic and other environmentally significant elements in Upper Pote River water, riverbank soil and riverbank garden vegetables irrigated using the water. Samples of Runhanga Cattle dip site soils, Upper Pote River water, Upper Pote riverbank garden soils and riverbank garden vegetables, were collected from 5 sites close to and along Upper Pote River, and were analyzed using ICP-MS. Data obtained confirmed contamination of Runhanga Cattle Dip site soils and Upper Pote river by 161.8 ± 0.7 $\mu g/kg$ and 8 ± 0.28 to 12.1 ± 0.28 $\mu g/kg$ As respectively. Arsenic levels in the river were highest close to the dip site, confirming leaching of As from the contaminated dip site. Arsenic was detected in all three vegetable species, at concentrations ranging from 9 ± 0.14 to 22 ± 0.1 $\mu g/kg$. The levels of As, as well as Cd, Cr, Cu, Fe, Hg, Mg, Mn, Sb and Zn, in the river water, riverbank garden soils and riverbank vegetables, fell within the permissible limits set by the WHO/FAO for food, irrigation water and soil respectively. However, the levels of Co in vegetable samples were above the set permissible limits and therefore, being highly toxic or carcinogenic, are cause for concern. Statistical correlation analysis confirmed that irrigating the garden soils with the Upper Pote River water had no significant effect on the concentration of As, or any of the metals studied, in the garden soils and the vegetable grown in the garden soils. Possible sources of the high levels of As, Co, Cd, Cr and Hg in the ecosystem are discussed.

Keyword: Arsenic; arsenic-based cattle dip; heavy metal; irrigation water; soil pollution; carcinogenic elements; cobalt.

1. INTRODUCTION

Arsenic (As) is a dangerous non-biodegradable substance classified as a Group I carcinogen in humans by the International Agency for Research on Cancer (IARC) (McLoon & Mason, 2003), the US Environmental Protection Agency (EPA) and the Agency for Toxic Substances and Disease Registry (ATSDR) (Abbas *et al.*, 2018). Continuous accumulation of arsenic in the human body causes several adverse effects including kidney damage, skin disorders, mental disorders, heart problems, and cancer (Jarup, 2003). It also results in the inactivation of some key enzymes.

Historically, arsenic was extensively used as a pesticide/acaricide in dip chemicals containing up to 14 to 22% of arsenic as As_2O_3 by weight, for the control of ticks throughout the world in the nineteenth century (Ellenberger and Chapin, 1919; Ramudzuli and Horn,

2014). In Southern Africa, As dip chemicals were used up to the early 1980s when they were banned (Mwatwara, 2014). In Zimbabwe most of the dip vats are situated close to rivers for easy access to water needed for replenishing the dip solution on a regular basis. In addition, disposal of the potent dip solution is by burying it into a pit as sludge, or pumping or scooping it on to the ground as run-off. Thus, dip sites that historically were based on As are potential sources of As pollution of the nearby rivers, and agricultural produce irrigated using water from such affected rivers. Leaching of As from cattle dip sites which were previously based on As has been reported several years after the use of As dip was discontinued (McLaren *et al.*, 1998; Ogunfowokan *et al.*, 2013).

Smallholder horticultural farming (SHF) is a major economic activity for villagers in areas near urban areas in Zimbabwe, to the extent that smallholder horticultural farmers are the major suppliers of fresh horticultural produce to urban populations (Tanyanyiwa and Bakasa, 2018). SHF is mostly carried out close to rivers and dams for easy access to fertile soils and water for irrigation. Thus, river pollution by As poses a health hazard to villagers near affected rivers and urban populations who consume SHF produce irrigated with such water. There is therefore need to monitor the levels of As in affected rivers and in riverbank small holder farm vegetables grown using irrigation water from such rivers.

A typical river vulnerable to As dip chemical contamination in Zimbabwe is Pote River. Pote River has its sources in the Domboshava area about 30 km north-east of Harare and flows northwards as shown in Fig. 1. Upper Pote River is the portion of Pote River shown in Fig. 1. Located about 30 m from the western banks of Upper Pote River, is Runhanga Cattle Dip (coordinates: ~ 80544N, 3025E, Fig. 1),

a dip vat that was historically based on As cattle dip, thus making the dip site a potential source of pollution for Upper Pote River by As as described above. Also locate about 1 km to the east are Molife Village and Molife Primary School.

Upper Pote River water is used by villagers living close the river for watering their domestic animals (cattle, goats, sheep and donkeys), and for irrigating smallholder riverbank vegetable gardens. The villagers consume vegetables and also sell some to urban dwellers in the City of Harare. Vegetables grown on contaminated soils have been found with high concentrations of heavy metals including As in Bangladesh (Heiken, 2006), Australia (Tom *et al.*, 2014) and the USA (McBride, 2013). The aims of this study were therefore to determine the elemental composition of Upper Pote River water, Upper Pote Riverbank garden soils and riverbank garden vegetables irrigated using the water, with a view to establishing whether the levels of As and other environmentally significant elements (Be, Cd, Cr, Co, Ni, Hg and Pb) fall within the FAO guidelines for irrigation water and for vegetables for human consumption. Preliminary studies carried out on Upper Pote River water in 2015, had shown high levels of As (17 – 161 μg/L) in the river water (Musiiwa and Zaranyika, 2015).

2. MATERIALS AND METHODS

2.1 Chemicals and reagents

The following were used: Nitric acid (55%), hydrogen peroxide (30%), hydrochloric acid (32%), hydrofluoric acid, all AR grade (Merck, South Africa); ULTRASPEC Multi-element Standard (ULTRASPEC, De Bruyn Spectroscopic Solutions, Kayalami, SA) containing 1000 μg/ml of each of the elements As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb[206], Pb[207], Pb[208], Sb and Zn; SADCMET S4 Proficiency Testing
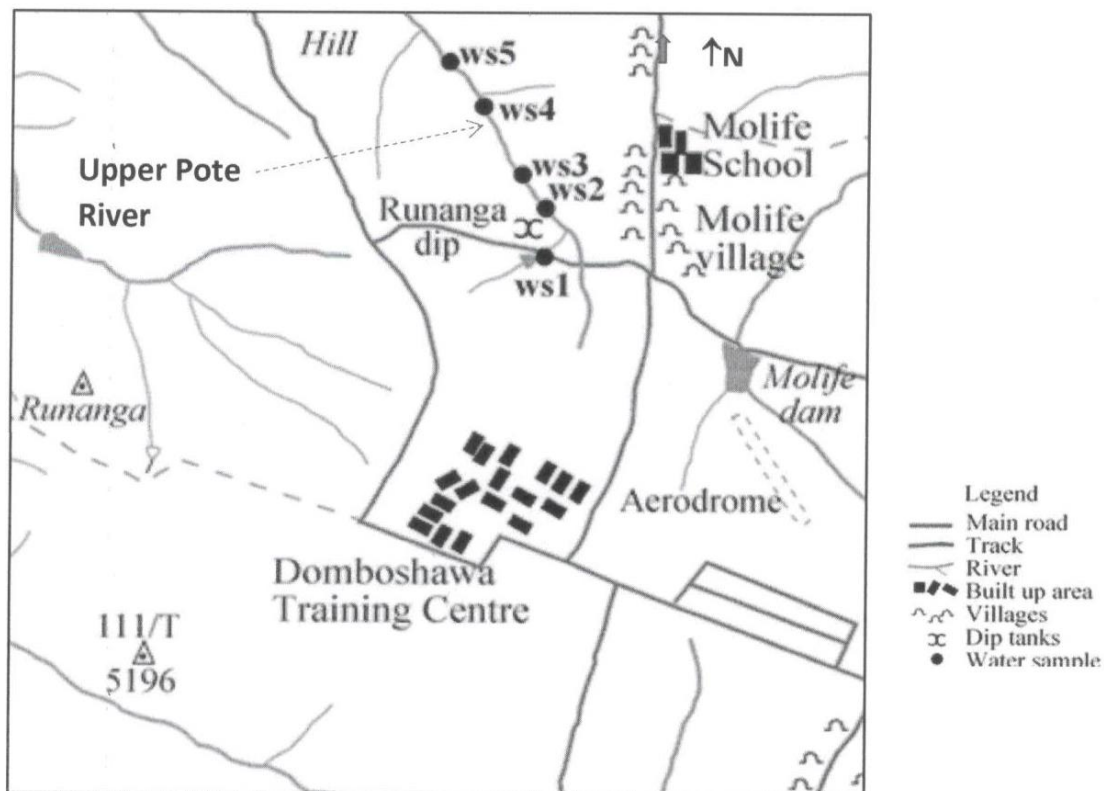
Sample for water (NamWATER LAB, Namibia).

Fig 1. Map showing Upper Pote River, Runhanga dip and Sampling Points (WS1-WS5).

2.2 Equipment

The following equipment were used: Inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent Technologies 7800, Agilent, South Africa), Microwave digester (Agilent Technologies Ethos, South Africa), analytical balance (CVL Toxicology Laboratory), pH meter (GAL Toxicology Laboratory, South Africa), and glassware (Erlenmeyer flasks, conical flasks, beakers, measuring cylinders, 100 mL volumetric flasks, polyethylene and Teflon beakers, and 1L plastic bottles) (GAL Toxicology Laboratory, South Africa).

2.3 Study site, sampling and sample pre-treatment

The study site, Upper Pote River, is found in the Domboshava area, Mashonaland East Province, Zimbabwe. Soils in the area are sandy with shiny feldspar grains and support sparse broom (*Myrothamnus flabellifolios*) and grassland vegetation (Nyamapfene, 1991). Temperatures usually range from 22 to 30 ºC in summer and may drop to freezing levels in winter (Chingombe et al., 2005; Mushore, 2013). The rain season often runs from November to April with rainfall ranging between 400 and 1150 mm, and precedes a dry season from May to October (Anusa, 2007).

Water and soil samples were collected from 5 sites situated at or close to sampling points WS1 to WS 5, at varying distances upstream and downstream of Runhanga dip site along Upper Pote River as shown in Fig. 1. Sampling point WS1 was a small dam about 100 m upstream of Runhanga dip. All the other sampling points were downstream of the dip along Pote River, and consisted of larger pools situated at the following approximate distances from the dip site: site WS2 about 200 m, site WS3 about

500 m, site WS4 about 1 km and site WS5 about 1.8 km. The profile of the river is such that the terrain around Sample Sites SW1 and SW2 is flat, but drops considerably, then levels off before Sample Site SW3.

Duplicate water samples were collected at each Sampling Site into 500 mL plastic bottles previously soaked in 10% HNO_3 for 24 hours and rinsed thrice with de-ionized water, then rinsed thrice with water to be sampled. The pH was measured on site using a pH meter (GAL Toxicology Laboratory, South Africa), previously calibrated using pH 4 and pH 9 buffer standards. Water samples were preserved with ultra-pure grade HNO_3 (Merck, South Africa) to pH 2 and stored in a refrigerator prior to analysis. Water samples were collected during October and November in 2019.

Soil samples from the vegetable gardens were collected in polyethylene bags which were previously soaked in 10% HNO_3 for 24 hours and rinsed thrice with de-ionized water. Soil samples were collected from the same locations as the vegetables, at a depth of approximately 10-15 cm (Okalebo *et* al. 2002). Five random samples were taken and then mixed together to obtain a composite sample for each garden sampled. The pH of each soil sample (Table 2) was measured upon arrival at the laboratory using a pH meter (GAL Toxicology Laboratory, South Africa) previously calibrated with buffer solutions of pH 4 and pH 9. Soil samples were dried in a forced air oven at 40 °C to remove moisture (Okalebo *et al.*, 2002). After the drying process, samples were sieved through a 2 mm sieve to remove large clumps of soil, and then stored in clean glass vials in a cool dry place pending analysis.

Soil samples from Runhanga dip site were also collected. Four random points around the dip vat, each approximately 2

m from the vat, were sampled and mixed to form a composite sample. The composite sample was then dried, sieved and stored in clean glass vials pending analysis.

Vegetable plant samples were collected from the riverbank gardens situated a few meters from the banks at each Sample Site along the river. Procedures for sample collection and sample treatment described by Okalebo *et al.* (2002) were followed. Vegetable species were sampled according to their availability, thus: *Lycopersicon esculentum* (tomato) was collected at Site SW1 and Site SW2, *Brassica oleracea ivar. acephala* (chomolia or covo in Zimbabwe) was collected at Site SW3 and SW4. *Brassica napus* (commonly known as rape) was collected at Site SW5. At each site edible parts of the plant were collected as follows: *Lycopersicon esculentum* (tomato), the tomato fruit; *Brassica oleracea ivar. Acephala* and *Brassica napus*, the edible leaves. Approximate distance of the gardens from the river at each site were as follows: site A, about 10 m; sites B and C, about 3 m; sites D and E, about 2 m. Harvesting of vegetables was done randomly in each garden. Samples were collected at five points a few meters apart, and combined to form a composite sample. The composite samples were appropriately labelled and stored in a refrigerator at 4 °C overnight, before they were cut to small pieces using a stainless-steel knife, and dried at 65 °C to constant mass in a forced air oven (Okalebo *et al.*, 2002). After the drying process, the samples were stored in clean glass vials in a cool dry place pending analysis.

2.4 Sample Preparation

The composite water sample (25 mL each) were pipetted into a 100 ml volumetric flask and made up to the mark with distilled water.

Soil samples (about 0.25 g each) were weighed accurately and placed into Teflon microwave digestion tubes previously rinsed with 10% nitric acid and deionized water. Two mL of 55% nitric acid, 6 mL of concentrated hydrofluoric acid and 2 mL of 32% hydrochloric acid were added to each digestion tube. The tubes were capped, placed on the microwave digester tube holder and the cap tightened using the cap spanner. The digestion tube holder was then placed into the Ethos Easy Advanced Microwave Digester (Agilent Technologies, South Africa), and the digester set to the soil digestion method, and digestion allowed to proceed for 45 minutes. The digestion tubes were opened in a running fume-hood to allow brown fumes to escape before the resulting digested soil sample solutions were transferred to clean ICP-MS sample tubes.

The dried vegetable samples (5 g each) were transferred to Teflon microwave digestion tubes pre-rinsed with 10% nitric acid and deionized water. Eight mL of 55% nitric acid and 2 mL of 30% hydrogen peroxide were added to each tube. The tubes were capped, placed on the digester holder and tightened with the cap spanner. The holder was placed into the Ethos Easy Advanced Microwave Digester (Agilent Technologies, South Africa) set to vegetable digestion method. After the 45-minute digestion, tubes were opened in a fume-hood to release brown fumes before transferring solutions to ICP-MS sample tubes.

2.5 Inductively coupled plasma–mass spectrometry (ICP-MS) analysis

The ULTRASPEC Multi-element Standard (ULTRASPEC, De Bruyn Spectroscopic Solutions, Kayalami, SA) was used to prepare standard solutions of the metals. A stock solution of 100 μg/g was first prepared from the multi-

element standard, then for Al, Cu, Cd, Ni, Cr, Mn, Pb, Zn, Fe and Co, three standard solutions 1 μg/g, 2.5 μg/g and 5 μg/g were prepared from the stock solution. For As, Hg, Se, and Sb three standards were made by first preparing a 10 μg/g composite stock solution of the elements then diluting to 0.01 μg/g, 0.05 μg/g and 0.1 μg/g.

The digested soil and vegetable samples were analyzed by directly injecting into the Agilent Technologies 7800 ICP-MS for elemental analysis. Water samples were similarly analyzed after dilution as discussed above. A reagent blank made up of 8 mL nitric acid and 2 mL hydrogen peroxide was also digested and similarly analyzed. Measurements were made in triplicate and analyzed statistically to obtain the mean and standard deviation. The results are shown in Tables 1 to 3.

2.6 Validation

Results were validated against a proficiency testing sample (SADCMET S4) for water. Quality control was assured by analysis of the blank and one of the standard solutions after every 5 measurements to ensure the accuracy of the instrument.

3 RESULTS

Tables 1 to 3 show the results obtained for the elemental composition of Upper Pote River water, Upper Pote Riverbank Garden soils along the river, and vegetables grown in the riverbank gardens using river water. The elements studied include Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, [206]Pb, [207]Pb, [208]Pb, Sb, Zn, in addition to As. The pH of the river water was slightly alkaline at 7.43±0.12 to 7.82±0.06 (Table 1), while that of the riverbank soils was acidic at 5.40±0.06 to 5.76±0.04 as a result of fertilizer application as shown in Table 2.

3.1 Runhanga dip site soils

The level of As in soil collected at the dip site was 161.8±0.7 μg/kg and was higher than the As levels for either the river water at 3.15±0.0.07 to 12.1±0.28 μg/kg (Table 1), or riverbank garden soils at 9.7±0.14 to 39.37 μg/kg (Table 2), and way above the FAO/WHO permissible limit for soils (*Codex Alimentarius Commission,* 2001a). Similar magnified quantities of As have been reported at disused dip sites in South Africa, Australia and New Zealand, (Okonkwo, 2007; Kimber et al., 2002; Sarkar et al., 2007). The dip site thus is a potential source of As pollution for the near-by Upper Pote River.

3.2 Upper Pote River water

The results for Pote River water (Table 1) show that As was detected at all five sampling points, at concentrations ranging from 3.15±0.0.07 to 12.1±0.28 μg/L, all within the International and FAO limit of 0.1 ppm (100 μg/L) for irrigation water (Ayers & Westcot 1994). Table 1 shows that As concentration in the river water was highest at sampling site SW2 closest to the dip site, confirming leaching of As from the dip site. The high level of As in soils at the dip site (161±0.0.7 μg/kg, Table 2) therefore means that As will continue to leach into the river for many years unless measures are found to reduce the level of As in the soils at the dip vat and its immediate surroundings. Figure 2 shows As accumulates downstream from the dip site due to reduced river flow rate.

As pointed out above, Sample Site SW1 is a small dam in the river about 100 m upstream of the Runhanga Dip site. The presence of As in the water sample collected at Sample Point SW1 points to pollution of the river upstream of the dip
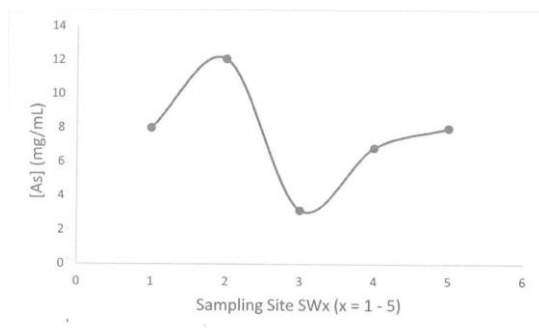
Fig 2, Concentration of arsenic (As) along Upper Pote River: SW1 – SW5

site by As, presumably from freshly dipped cattle grazing in the area surrounding the dam and drinking water in the small dam. Cadmium, Cr and Hg could not be detected in water samples from any of the five sampling points, while the rest of the elements studied were detected at all the sampling points. The levels measured were all within the International and FAO limits (Ayers and Westcot, 1994) (see Table 1).

3.3 Riverbank garden soils

The concentration levels of As in the riverbank garden soils at 9.7 ± 0.14 to 39.37 μg/kg (Sampling sites SW1 to SW5, Table 2), are higher than the As levels for the river water ($3.15\pm0.0.07$ to 12.1 ± 0.28 μg/kg). For all the other elements, the results for the sample collected at the dip site and those for the garden soils are comparable. Of all the elements studied, permissible limits in soil have only been specified for As, Cd, Hg and Pb as shown in Table 2 (Monchanin, 2021; Codex Alimentarius Commission.2001b), and in all cases the levels measured fall within these limits.

3.4 Riverbank garden vegetables

The results for the riverbank garden vegetables (Table 3) show that all 12 elements studied were detected in all

three vegetable species studied, *L. esculentum*, *Brassica oleracea var. acephala*, and *Brassica napus*, and at all five Sampling Points, except for (a) Cr which was detected at Sampling Point SW2 in *L. esculentum*, and at Sampling Point SW3 in *Brassica oleracea var. acephala,* and Hg which was detected at Sampling Point SW4 in *Brassica oleracea var. acephala,* and at Sampling Point SW5 in *Brassica napus*. Arsenic was detected in all three vegetable species, at concentrations ranging from 9 ± 0.14 to 22 ± 0.1 μg/kg, all within the international limit of 0.1 – 0.2 mg/kg (Codex Alimentarius Commission, 2014). The levels of all the other elements studied fall within the limits specified by FAO/WHO (1989, 2008), except for Co which at 22.15 ± 0.21 to 48 ± 0 μg/kg, exceeded the set limit of 0.01 mg/kg (FAO/WHO, 2008) at all five sampling points, i.e., for all three vegetables species sampled. Cobalt is a known carcinogen (Beyersmann, 2002; Bal and Kasprzak, 2002; Chernova et al., 2012; Arita et al., 2012), hence these high results for Co are cause for concern.

3.5 Elemental levels in Upper Pote River: Impact on Upper Pote riverbank garden vegetables

Statistical correlation analysis (Table S1) between the concentrations of the elements studied in Upper Pote River water, and concentrations in riverbank soils and vegetables grown in the riverbank garden soils, shows that there is no significant correlation (at $p \leq 0.05$ or $p \leq 0.1$) between the concentration of any of the elements studied in Upper Pote River water and the concentrations of the same elements in the riverbank garden soils, or vegetables grown in the riverbank garden soils, confirming that Upper Pote River water, and hence leachate from the contaminated

Table 1. Levels of heavy metal (µg/L) (mean±SD, n = 3) in water, Upper Pote River, Mashonaland East Province, Zimbabwe. (SD = standard deviation)

METAL	Sample Site[a]					RMC[b]
	SITE SW1	SITE SW2	SITE SW3	SITE SW4	SITE SW5	
As	8±0.28	12.1±0.28	3.15±0.07	6.85±0.07	8±0	0.1
Cd	ND	ND	ND	ND	ND	0.01
Co	0.7±0.42	13±0	345.5±0.71	0±0.07	122±1.41	0.05
Cr	ND	ND	ND	ND	ND	0.1
Cu	14.9±0.14	2.3±0.7	0±0.28	6.3±0.7	0.15±0.07	0.2
Fe	479549.5±0.7	493363.5±0.7	803222.5±2.1	52876.5±3.5	425764±0.7	5
Hg	ND	ND	ND	ND	ND	-
Mg	536.5±0.7	593±0	1042±1.41	279.5±0.7	637.5±0.7	-
Mn	8711±2.82	49326±1.41	42368.5±2.1	2269.5±0.7	10100.5±0.7	0.2
Ni	12±0.28	0.25±0.21	1.1±0.28	4.95±0.07	0.1±0.28	0.2
Pb [206]	23.1±0.28	25±0.14	3.85±0.07	58.6±0.99	0±0	-
Pb [207]	22.9±0.28	2.9±0.28	52.85±0.21	0±0	0±0	-
Pb [208]	23±0	3.05±0.07	55.05±0.07	0.5±0.71	0.25±0.07	-
Pb[c]	69.0	30.95	111.75	59.1	0.25	5.0
Sb	35.15±0.35	220.5±0.71	0.15±0.21	0±0.14	0.7±0.42	-
Zn	143±1.41	0±0	28.55±3.5	0.65±0.49	0.05±0.07	2.0
pH	7.43±0.12	7.28±0.06	7.82±0.06	7.56±0.03	7.73±0.29	

[a]See Fig.1; [b]RMC = Recommended maximum concentration in irrigation water (Ayers and Westcot, 1994). RMC based on a continuous water application rate at one site consistent with good irrigation practices (10000 m3 per hectare per year). The RMC should be adjusted downward accordingly. If the water application rate is greatly exceeded, but no adjustment should be made for application rates less than 10 000 m3 per hectare per year. [c]Pb = $\sum Pb^x$ (x = isotopic mass). ND = not detected. (*) = exceeds set limits.

Table 2 Mean concentration of heavy metals (µg/kg, n = 3) in soil samples collected at Runhanga dip site and from riverbank gardens along Upper Pote River, Mashonaland East Province, Zimbabwe

Metal	Sample Site[a]						Permissible limits (ppm)[b].
	Dip Site	Site SW1	Site SW2	Site SW3	Site SW4	Site SW5	
As	161.8±0.7	39.37±0.1	20.2±0.04	16.4±0.	9.7±0.14	18.9±0.2	20
Cd	22.1±0.14	28±0	16.1±0.7	14.1±0.17	18.05±0.1	20±0.1	0.9 - 3
Co	34.7±2	62.3±0.02	63.9±0.07	27.3±0.7	49.6±0.07	20.9±0.14	
Cr	3.11±0	18.9±0.12	15.8±0.07	15.5±0.15	6.18±0.02	32.7±0.7	
Cu	96.73±0.07	102.4±0.3	91.6±0.14	149.5±0.7	128.2±0.1	129.6±0.07	
Fe	47000±0.02	59390.5±0.07	314465.5±0.4	667828.5±0.7	224146±0	114841.5±0.1	
Hg	ND	ND	20.7±0.14	97.7±0.14	88.15±0.2	61.7±0.2	0.03 - 2
Mg	ND	9283.5±0.4	8422.5±0.7	6346±0	10224.5±0.1	9136.5±0.7	
Mn	2140.8±0.13	11291.6±0.3	59921.8±0.14	239330±0	64581.2±0.7	388771.5±0.5	
Ni	3.4±0.07	116.6±0.7	44.5±0.2	53.91±0.1	89.9±0.3	168.6±0.2	
^{206}Pb	17.1±0.7	15.1±0.07	25.75±0.14	41.06±0.2	24.8±0.4	19.9±0.6	
^{207}Pb	19.9±0.2	ND	8.57±0.7	15.7±0.4	8.6±0.2	13.5±0.1	
^{208}Pb	17.6±0.4	ND	9.03±0.1	15.6±0.14	9.0±0.1	12.8±0.2	
Pb[c]	54.6	15.1	43.35	72.36	42.4	46.2	30 - 50
Sb	16.6±0.06	16.9±0.07	10.3±0.14	13.7±2	62±0.14	90.4±0.14	
Zn	484.4±0.14	89.1±0.7	265.4±0.07	243.9±0.7	194.8±0.2	180.3±0.1	
pH		5.40± 0.06	5.76±0.04	5.76±0.04	5.66±0.06	5.59±0.06	
Fertilizer[c]		Phosphate	(a) Phosphate (b) Compost	Phosphate	(a) Phosphate (b) Compost	(a) Phosphate (b) Cattle manure	

[a]See Fig. 1; [b]International Permissible limits (Codex Alimentarius Commission*, *2001b); [c]Pb = ∑Pb^x (x = isotopic mass). ND = not detected. [c] Responses supplied by the farmer at each riverbank garden to a questionnaire on the type of fertilizers applied.

Table 3 Mean concentration of heavy metals (μg/kg, n=2) in vegetables grown in riverbank gardens along Upper Pote River, Zimbabwe

Metal	Sample site[a] (Vegetable plant species)					Int. limits (ppm)[b]	WHO (mg/kg)[c]
	Site SW1 (*L.esculentum*)	Site SW2 (*L.esculentum*)	Site SW3 (*oleracea var. acephala*)	Site SW4 (*oleracea var. acephala*)	Site SW5. (*napus*)		
As	9±0.14	16.15±0.07	11±0.14	22±0.1	13.95±0.1	0.1–0.2	
Cd	22.95±0.07	4.05±0.07	2.05±0.1	5.45±0.07	2.05±0.07	0.05-2	
Co	23±0*	35.05±0.07*	22.15±0.21*	48±0*	24.15±0.21*		0.01[d]
Cr	ND	6.05±0.07	10.15±0.21	ND	ND		-
Cu	90.95±0.2	157±0	94.8±0	80.3±0.7	17±0.14		73.3[c]
Fe	107912±1.41	157485.5±2	140673.5±0.7	366013.5±0.7	15702±1.41		425.5[c]
Hg	ND	ND	ND	20.15±0.1	13.25±0.07	0.5-1	0.03[d]
Mg	1655±0	1676.1±0.14	6602.5±0.71	8703.5±0.7	3276±0		-
Mn	59987.5±0.7	8274±0	1200±0	20936±0	794.5±0.7		-
Ni	27.15±0.07	6.95±0.07	34.05±0.07	6±0.14	0.95±0.1		67.9[c]
Pb[206]	2.05±0.21	0.05±0.07	5±0.14	0.15±0.1	16.9±0		
Pb[207]	2.15±0.07	0.05±0.1	4.85±0.21	17.15±0.1	14.95±0.1		
Pb[208]	2±0	0.1±0.14	5.485±0.07	22±0	15±0		
Pb[e]	6.2	0.2	15.335	39.3	46.85	0.01-3	0.3[c]
Sb	13.05±0.07	41.25±0.07	24.05±0.1	46±0	10.05±0.07		-
Zn	35±0	51.25±0.1	42±0	95.4±0.14	35.1±0.14		99.4[c]

[a]See Fig.1; [b]International Permissible limits in Food (Codex Alimentarius Commission, 2015). [c]WHO, 1989; [d]WHO, 2008.   [e]Pb = $\sum Pb^x$ (x = isotopic mass). ND = not detected. (*) = exceeds set limits.

site, has no significant impact on elemental levels in the riverbank soils or the vegetable grown therein. This conclusion is supported by the fact that the concentrations of Cd, Cr and Hg in the riverbank soils were high at 14.1±0.17 to 28±0 μg/g, 6.18±0.02 to 32.7±0.7 μg/g and 0 to 97.7±0.14 μg/g respectively, whereas their concentrations in the river water fell below the limit of quantification of the analytical method employed (Table 1), showing that the source of these elements in the riverbank soils cannot be the river water used for irrigating the riverbank soils.

Possible sources of As in the garden soils are historical pollution by arsenic dip from freshly dipped cattle grazing in the area before the use of As dip was discontinued, and fertilizers applied by the riverbank garden farmers. If historical arsenic cattle dipping is the source, then cattle were major dispersal agents for As, as they roamed freely across land surrounding dip sites for several km. Thus, soil pollution from historical cattle dipping may be more widespread than currently thought. There is therefore a need for a survey to assess the level and extent of soil and river pollution by As throughout Zimbabwe.

In regard to possible pollution from fertilizer application, all the farmers indicated, in response to a questionnaire given to them prior to sample collection, that they all apply phosphate and organic fertilizers to their crops as shown in Table 2, in order to increase yields. Several workers have reported high levels of heavy metals in phosphate and organic fertilizers (Al-Misri et al., 2004; He et al., 2005; Lopez et al.,

2007; Saueia et al., 2013; Ogabiela et al., 2009), while Stacey et al. (2010) reports that both types of fertilizers are known to contain high concentrations of toxic metals which include Co, Cd, As, Cr, U, Pb and Ni. This may explain the source of these elements in Upper Pote riverbank garden soils and riverbank garden vegetables, including the high levels of Co encountered in the vegetables in this study (Tables 1 and 3). Further work is therefore required to confirm whether fertilizers used by the farmers are indeed the source of the high levels of these metals in Upper Pote River ecosystem.

The work reported in this article is significant as it is the first time the impact of the historical use of As cattle dip in this country has been studied. Follow-up work to establish the level and extent of soil and river pollution by As, and the associated risk to humans and domestic animals, is strongly recommended. The discovery that the level of Co in the riverbank garden vegetables exceeds the WHO/FAO set limit is also significant, hence follow-up work is also recommended in order to establish its source and possible remedial measures that can be taken.

4. CONCLUSIONS

From the foregoing discussion the following conclusions can be made: (i) Although the use of As-based dip was discontinued in the early 1980s in Zimbabwe, the Runhanga cattle dip site is still contaminated with As of up to 161 μg/kg. (ii) Likewise, the nearby Upper Pote River is contaminated with As ranging from $3.15\pm0.0.07$ to 12.1 ± 0.28 μg/L, as a result of arsenic leaching from the polluted dip site soils. (iii) Irrigation of riverbank vegetable garden soils with Upper Pote River water, however, has no significant impact on the levels of As, as well as other toxic heavy metals, in the riverbank garden soils and vegetables grown in them. (iv) The levels of Co, a known carcinogen, exceeded the limit of

0.01 μg/g specified by FAO/WHO for food in all three riverbank garden vegetable species studied (*L. esculentum, Brassica oleracea var. acephala,* and *Brassica napus*), which is cause for concern, and hence requires further investigation to establish the source of the Co contamination.

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