The reach of human health risks associated with metals/metalloids in water and vegetables along a contaminated river catchment: South Africa and Mozambique

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Highlights

• Extent of water pollution impacts on the health of indigent communities in South Africa and Mozambique was investigated.

• Heavy metals were measured in locally grown vegetables and water from the river consumed by households.

• Several metals/metalloids exceeded the World Health Organization guidelines for safe levels of intake by water ingestion

• Arsenic in water samples posed the highest cancer risk.

• Potential to cause adverse human health impacts from direct use of untreated river water is evident in both countries.

ABSTRACT

Background: Anthropogenic pollution was identified as an environmental problem of concern when, in 2008, dozens of crocodiles died in the Olifants River catchment near the border of South Africa and Mozambique. Given the close proximity of households to the river and their making use of river water, we aimed to determine to what extent water pollution has an impact on health of indigent communities in South Africa and Mozambique in the catchment area.

Methods: Water and vegetable samples were collected from the study areas. Biota samples were washed with double de-ionized Milli-Q water and freeze-dried. Heavy metal analyses in water and vegetables were done by means of Inductively Coupled Plasma Optical Emission Spectroscopy. Metal concentrations were applied in a human health risk assessment to estimate health risks.

Results: Mean concentrations of antimony, arsenic, cadmium, chromium, mercury, molybdenum, nickel and selenium in water samples from South Africa exceeded the World Health Organization guidelines for safe levels of intake. Only iron exceeded the recommended guidelines in water samples from Mozambique. Metals/metalloids were found in lower concentrations at Mozambique sites downstream of South African sites. In vegetables, uranium was between 10-20 times above safe guidelines in South Africa and between 3-6 times in Mozambique. Arsenic in water samples posed the highest cancer risk.

Conclusions: Even with a reduction in the metal concentrations in river water from South Africa to Mozambique, the potential to cause adverse human health impacts from direct use of polluted river water is evident in both countries.

Keywords:

Environmental water pollution

Human health risk assessment

Metals &/ metalloids

Vegetables

Catchment

1. Introduction

Poor water quality has significant impacts on human health including those related to microbes and vectors such as infectious diarrhoea, repeat or chronic diarrhoea and those related to chemical species which can contribute to non-diarrhoeal diseases (Hunter, MacDonald and Carter, 2010). Arsenic, mercury and uranium are three metals/metalloids which have significant associations with adverse health effects. Arsenic is a 'known human carcinogen' (Class A: Known human carcinogen) and can accumulate in the body (ATSDR, 2017). Chronic effects include skin lesions, hyper-pigmentation and cancer of the skin and internal organs, while acute effects can be death from upper respiratory, pulmonary, gastrointestinal and cardiovascular failure. Nerve damage and sensory loss in the peripheral nervous system is a primary symptom of arsenic poisoning. Mercury causes neurological (organic mercury) and renal disturbances (inorganic mercury) where the former is more toxic than inorganic mercury (ATSDR, 2017). Mercury is classified as Class D: Not classifiable as to human carcinogenicity. Uranium is a radioactive substance which, if ingested in large concentrations, can cause kidney disease (nephritis) and possible reproductive effects (ATSDR, 2017).

The Olifants River has been described as one of the most polluted rivers in southern Africa as a result of anthropogenic impacts that affect water quality (Grobler et al. 1994). The sources of pollution include mining, coal-fired power stations, industrial activities, agriculture as well as inadequate treatment of wastewater (Dabrowski et al. 2008; Hobbs et al. 2008; DWA 2011). Several years ago, wildlife deaths in the Olifants River Catchment Management Area alerted scientists to possible serious water pollution problems. It was suspected that communities living in close proximity to the river were also exposed to the pollution, but to what extent and whether health problems could be attributed to this exposure were unknown. Initially, environmental monitoring was carried out to characterise water pollution in this intense mining and agricultural area (Oberholster, 2010). However, water ingestion is only one exposure pathway; consumption of vegetables watered with river water is another pathway. Metals accumulate in plants, either through uptake via the roots from the soil, or by irrigation with untreated river water; previous studies have shown that heavy metal contamination of fresh produce is a significant human health risk (Chaney et al. 1999; Khan et al. 2008; Sipter et al. 2008; Amin et al. 2013). Many studies have found that accumulation of trace metals in edible plants may pose a risk to both human and animal health (Gupta and Gupta, 1998; McBride, 2007; Monika and Katarzyna; 2004; Adriano, 2001; McLaughlin et al., 1999; Pruvot et al., 2006).

The purpose of this study was to determine to what extent water pollution may have an impact on the health of indigent communities in South Africa and Mozambique in the Lower Olifants River catchment area. The study areas included villages near Hoedspruit in Limpopo Province (South Africa) and communities around Lake Massingir in Mozambique (Figure 1). Personal exposure to environmental pollution was identified during a pre-study visit as being via ingestion (drinking) of untreated river water and consumption of vegetables watered with river water. Community members in the South African study site often made use of the river water for drinking and washing, and some households maintained vegetable gardens for fresh produce. In Mozambique, there was extensive use of Lake Massingir's water, and crops were planted adjacent to the water and irrigated from the lake. The community also acquired their drinking water directly from the lake. The study objectives were therefore (1) to measure metals / metalloids in locally grown vegetables and water from the river and / or lake consumed by households living close to the river in the two countries; and (2) to assess potential non-carcinogenic and carcinogenic (where risk metrics were available) health risks of metals/metalloids based on levels of metals/metalloids detected in samples taken from consumed vegetables and ingested water.

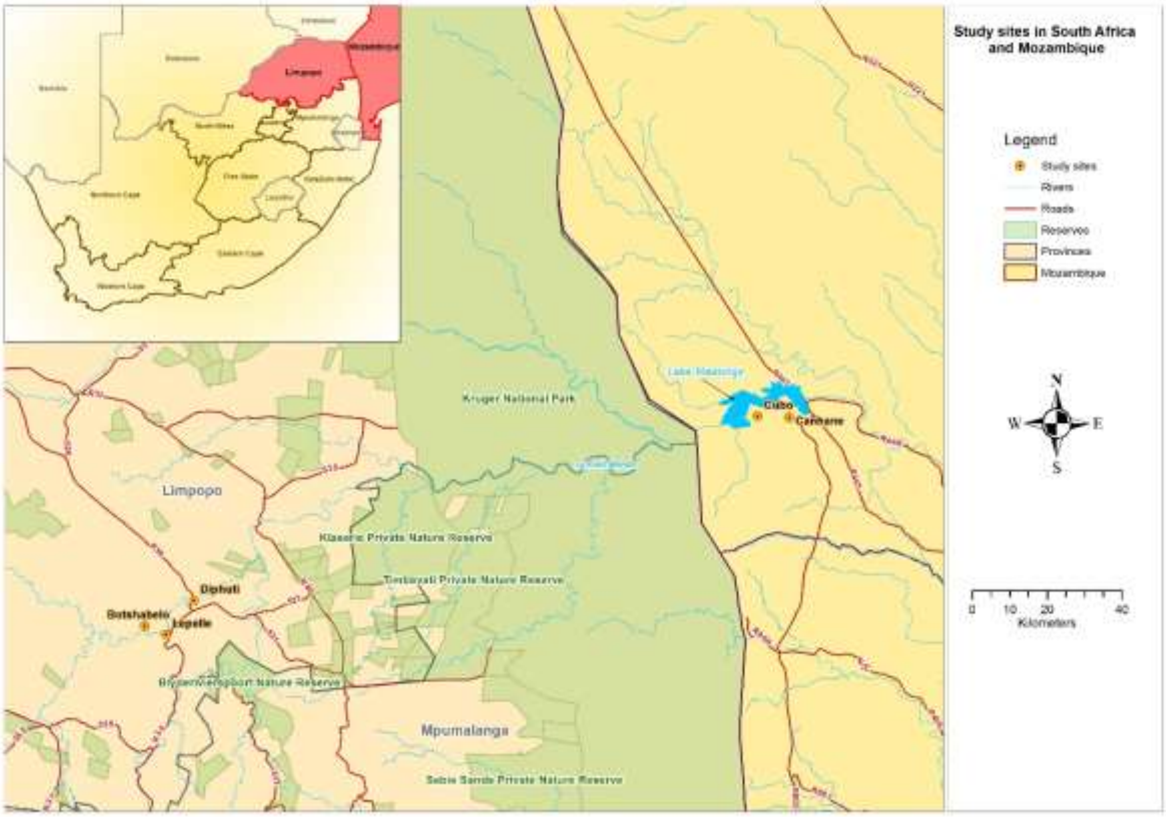

Fig. 1. Map of study sites and locality in South Africa and Mozambique.

2. Materials and methods

2.1. Sample and study sites

Water and vegetable samples were collected from the study areas (Figure 1) between December 2012 and May 2013. The South African sites are in river-dependent (Olifants River) communities while the Mozambican sites are in lake-dependent communities. The Olifants River flows through one of the geographically largest nature conservation areas in Southern Africa.

Each of the study areas, i.e. Lepelle, Botshabelo and Diphuti in South Africa; Canhane and Cubo in Mozambique, were visited twice to collect samples. The Lepelle and Botshabelo areas (situated in the Limpopo province, South Africa) were visited in December 2012, and then again in May 2013. The two settlements in Mozambique, i.e. Canhane and Cubo, were visited in February and May 2013. Research ethics clearance for the study fieldwork was granted by the Council for Scientific and Industrial Research Council Ethics Committee (8 October 2012 Number 44/2012).

Water and sediment samples were collected during the first site visit to each area, while water, sediment and vegetable (locally produced) samples were taken during the second sampling visit. The sample numbers were limited due to financial constraints and the high cost of analysis. Water samples were collected from environmental water sources at locations from where residents collected water, or had easy access to the water (for instance, a boat launch site or a drinking water collection/extraction point). These locations were pointed out to the research team during local group discussions. The surface water sampling was performed as per the guiding principles and procedures given in the Surface Water Sampling operating procedure published by the U.S. EPA (USEPA, 2013). Water from each sampling point was collected in both glass and plastic containers in order to satisfy different test requirements. One litre heat-sterilized Schott bottles (Duran, Germany) and newly manufacture non-reusable 1 litre plastic containers (Plastilon, South Africa) were utilized throughout the study. The sample containers were rinsed several times with the water from the sampling point, where after water was sampled using the dipping technique (in accessible areas) or else using a scoop in challenging locations. Soil and sediment samples were collected from the sediment surface layer (in lake or river settings), or 100 mm below surface for soil samples taken from arable land. Sterile 150 mL specimen containers (Plastpro Scientific, South Africa) were used to collect and transport the soil and sediment samples. Locally grown (i.e. in the settlement) vegetables were not easily found in the South African study sites of Lepelle and Botshabelo as very few residents practiced subsistence farming. At these sites, the research team sampled as many different types of vegetables as were available on the day of sample collection. In Canhane and Cubo, the residents relied more on subsistence farming and each village had a local produce market. Vegetables, produced locally, were purchased from the local market, with the limiting factor again being the variety that was present on the day of sample collection. Vegetables were sealed individually in plastic zip-lock bags (Glad, South Africa) for transport to the laboratory. All samples (water, sediment/soil, vegetables) were kept cool (5-15 °C) during transit and storage.

2.2. Sample analysis

All water and vegetable samples were analysed for the following metals /metalloids which have been classified by the International Agency for Cancer Research as carcinogenic, or yet to be classified (except for iron which is considered non-carcinogenic): aluminium, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, selenium, strontium, titanium, uranium, vanadium and zinc (a summary of documented health effects of all contaminants is provided in Table S1). Metal analyses were done on acidified (5% nitric acid) and filtered water samples (0.45um) by means of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrumentation (Thermo ICap 6500 Series Inductively Couple Plasma Optical Emission Spectrometer) following the approved analytical methods detailed in “Standard Methods for the Analysis of Water and Wastewater” (APHA, 2017). The following reference materials were used for the various sample types. Freshwater standards: Certipur Certified Reference Material ICP multi-element standard IV traceable to international NIST SRM, produced by Merck KGaA, Frankfurter Germany. Soil reference material: PACS-3 Marine Sediment Certified Reference Material for Trace Metals and other Constituents, produced by National Research Council Canada. Biota reference material used was TORT-3 Lobster Hepatopancreas Reference Material for Trace Metals produced by National Research Council Canada.

The biota samples were randomly sampled (one carrot, one spinach etc.) and a weighed amount was freeze dried. Sediment samples were freeze-dried in a Virtis Freeze mobile 12, ball-milled in Retsch Planetary Ball mill then acid digested in a closed vessel MARS X microwave assisted digestor. Acid digestates were diluted with Milli- Q doubly deionised water before being analysed by ICP-OES (Thermo ICap 6500 Series Inductively Couple Plasma Optical Emission Spectrometer).

Sample metal concentrations were applied in a human health risk assessment (HHRA) to estimate non-carcinogenic and carcinogenic health risks posed by ingestion and consumption of water and vegetables. Half the detection limit was used when handling non-detects of certain metals in some samples.

2.3. Human health risk assessment (HHRA) model

HHRA is the process used to estimate the nature and probability of adverse health effects in humans who may be exposed to hazards in contaminated environmental media now or in the future (USEPA, 2012). The hazards can be chemical, physical, microbiological or physiological. HHRA consists of four stages - hazard identification, exposure assessment, dose response (toxicity) and risk characterization (Figure S1). This study looked at the exposure of populations to chemical contaminants in the form of metals/metalloids via the consumption of vegetables and ingestion of water. HHRAs for both vegetable and water samples were calculated using mean and 95th percentile values of heavy metal concentrations in the samples per site.

2.4. Water health risk assessment

Dietary exposure to metals/metalloids through ingestion of water was obtained by using *Equation 1*:

$$ADD = \frac{C(m) \times IR}{BW}$$ *(Equation 1)(USEPA, 2011)*

Where:

ADD	=	Average Daily Dose
IR	=	daily intake rate (2L/day)
C	=	metal concentration in water samples (mg/L)
BW	=	average adult body weight (70kg)

2.5. Vegetables health risk assessment

Dietary exposure to metals/metalloids through consumption of vegetables was obtained by calculating the Average Daily Dose (ADD) using *Equation 1* (USEPA, 2011) where:

IR	=	food ingestion rate (240g/person/day)

C	=	metal concentration in food samples (mg/kg)
BW	=	average adult body weight

2.6. Non-carcinogenic health risks

Non-carcinogenic health risks of exposure to individual metals/metalloids were represented as a hazard quotient (HQ) which is a unitless value that is calculated using the *Equation 2* from the USEPA (2011):

$$HQ = \frac{ADD}{RfD}$$ *(Equation 2)* (USEPA, 2011)

Where:

RfD	=	oral reference dose of the heavy metal

A value for HQ below 1 means that the exposed population is unlikely to experience adverse health effects and an HQ value greater than 1 represents a potential health risk to the exposed population (USEPA, 2000).

2.7. Carcinogenic risk calculation for water and vegetables

For calculating the theoretical excess cancer risk for exposure to carcinogens, a Life-time Average Daily Dose (LADD) was calculated for both water ingestion and vegetable consumption using *Equation 3* and *Equation 4* as follows:

$$LADD = ADD \times \frac{ED}{Lft}$$ *(Equation 3)*

And

$$Risk = 1 - e^{-(\beta \times LADD)}$$ *(Equation 4)*

Where:

ED	=	exposure duration (30 years)
Lft	=	lifetime (days)
β	=	oral potency factor (USEPA, 2011)

Equation 4 can be simplified and approximated using *Equation 5*.

$$\text{Risk} = \text{LADD} \times \beta \qquad \textit{(Equation 5)}$$

The risk estimates represent the theoretical excess cancer risk. This is the risk of developing cancer in addition to the background cancer incidence. For example, if the cancer risk is found to be $1 \times 10^{-4} = 0.0001 = 1/10\ 000$, then it can be said that there is an excess risk of developing cancer of 1 in ten thousand. The World Health Organization (WHO, 2003) defines the acceptable risk level as "an estimated upper-bound excess lifetime cancer risk of one additional cancer per 100 000 of the population ingesting drinking water containing the substance at the set guideline value for 70 years (life expectancy)". Thus, the World Health Organization (WHO, 2004) and several countries world-wide have set their acceptable cancer risk level at 10^{-5} (or 1 in 100 000). Carcinogenic and non-carcinogenic risks were calculated using reference doses (*RfD*) and cancer slope factors (*CSF*) obtained from the sources listed in Table S2.

2.8. Statistical analyses

Statistical analyses were performed using Stata™ Version 14 (StataCorp, 2015). A one-way analysis of variance (ANOVA) test for differences between study site means was performed to test whether or not differences in metal concentrations in vegetables and water samples between study sites were statistically significant.

3. Results

3.1. Water and vegetable sample metal results

A total of 39 samples were collected during the sampling campaign of which 23 were from South Africa and 16 were from Mozambique. Of the total, 16 were water samples and 23 were vegetable samples, with 7 and 9 from Mozambique, and 9 and 14 from South Africa, respectively. Metal concentrations were mostly higher in South African samples compared to Mozambican samples of both water and vegetables, with one exception being the mean iron concentration in water samples in Mozambique (Figure 2, Supplementary Table S3). Strontium concentration in water samples in South Africa had the greatest variability.

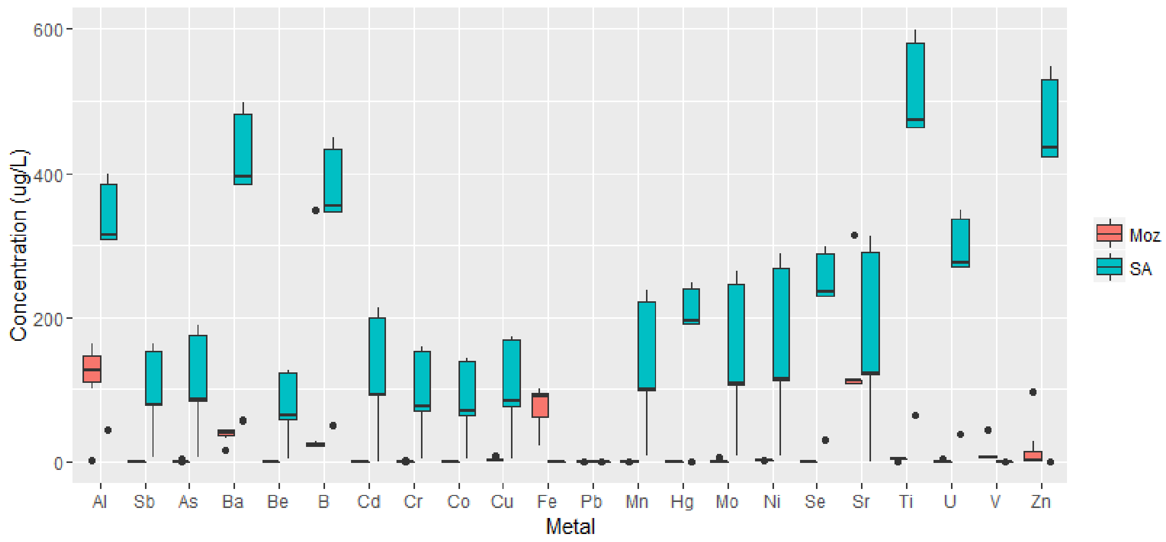

Fig. 2a. Metal/metalloid concentrations (μg/L) in water samples in South Africa and Mozambique. Top whisker: greatest value excluding outliers; Upper quartile: 25% of the data greater than this value; Median: 50% of data is greater than this value; Lower quartile: 25% of the data are less than this value; Bottom whisker: minimum value excluding outliers.

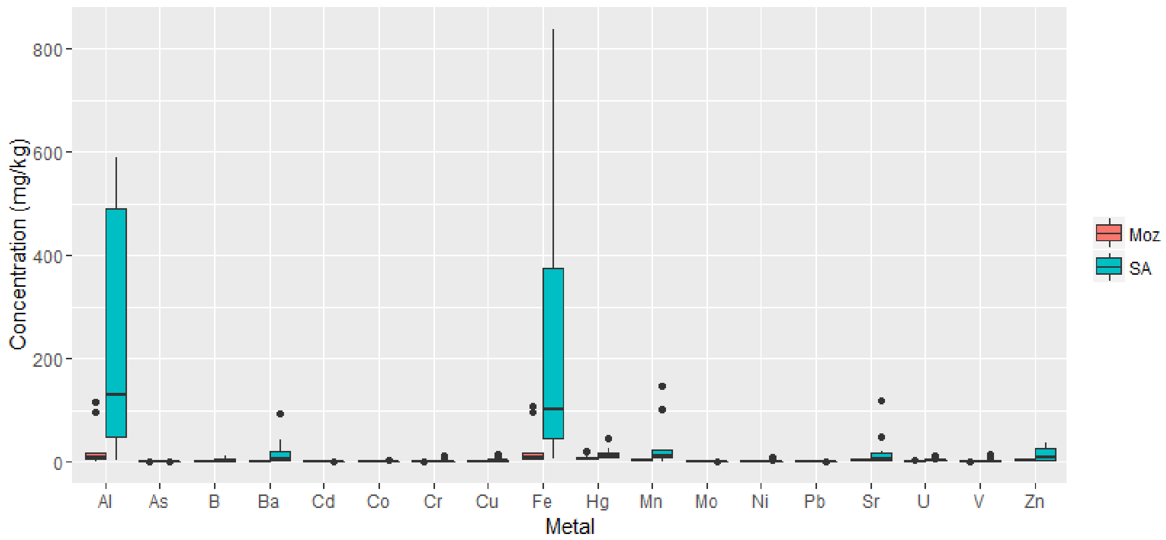

Fig. 2b. Metal/metalloid concentrations (mg/kg) in vegetable samples in South Africa and Mozambique. There are no guideline values for alumimium, strontium and vanadium but the results are shown nonetheless.

3.2. Exceedance of maximum recommended concentration in water samples

The mean concentrations of several metals/metalloids in water samples from South Africa exceeded the guidelines for safe levels of intake as recommended by the World Health Organization (WHO, 2008). These included antimony, arsenic, cadmium, chromium, mercury, molybdenum, nickel and selenium (Table S4). Only the concentration of iron exceeded the recommended guidelines in water samples from Mozambique (WHO, 2008).

3.3. Exceedance of maximum recommended concentration in vegetable samples

For vegetable samples in South Africa, iron was the only metal that had a mean concentration above the maximum recommended level (Table S3). The levels of the remainder of the metals/metalloids in vegetable samples in both countries were below the maximum recommended levels.

3.4. Statistical analyses for differences in metal concentrations between country sites

A one-way ANOVA was conducted to determine whether or not there were statically significant differences for heavy metal concentrations in water and vegetable samples between the sites in South Africa and Mozambique (Table S5). The ANOVA results are presented as boxplots in Supplementary Figure S2. For the drinking water samples (Figure S2a), the greatest statistically significant differences between the two countries were for selenium, titanium and uranium (F = 27.57, 27.34 and 27.79, p = 0.0001, respectively). For the vegetable samples (Figure S2b), the highest statistically significant difference between the two countries was for zinc (F = 7.25, p = 0.0136). Overall, metal concentrations in both water and vegetable samples in South Africa were higher than those in Mozambique although there are overlaps for some metals/metalloids. The boxplots also show that there are large variations in mean metal concentrations in water and vegetable samples among the countries.

3.5. Calculated non-carcinogenic health risks from water ingestion

ADD values for the ingestion of drinking water from the South African and Mozambican sites are given in Table S6. The estimated ADD values for metals/metalloids (marked with *) in water samples in South Africa were above their reference doses. However, the ADD values for metals/metalloids in water samples from the Mozambican sites were all below their reference doses. The HQ values for water samples from South African sites are provided in Figure 3a. Mercury had the highest HQ for water samples from both Lepelle and Botshabelo. All the HQ values for water samples collected from the Mozambican sites (as they pertain to metals/metalloids) were below 1 (Figure 3b), therefore no adverse non-carcinogenic effects can be expected from drinking water collected from those sites.

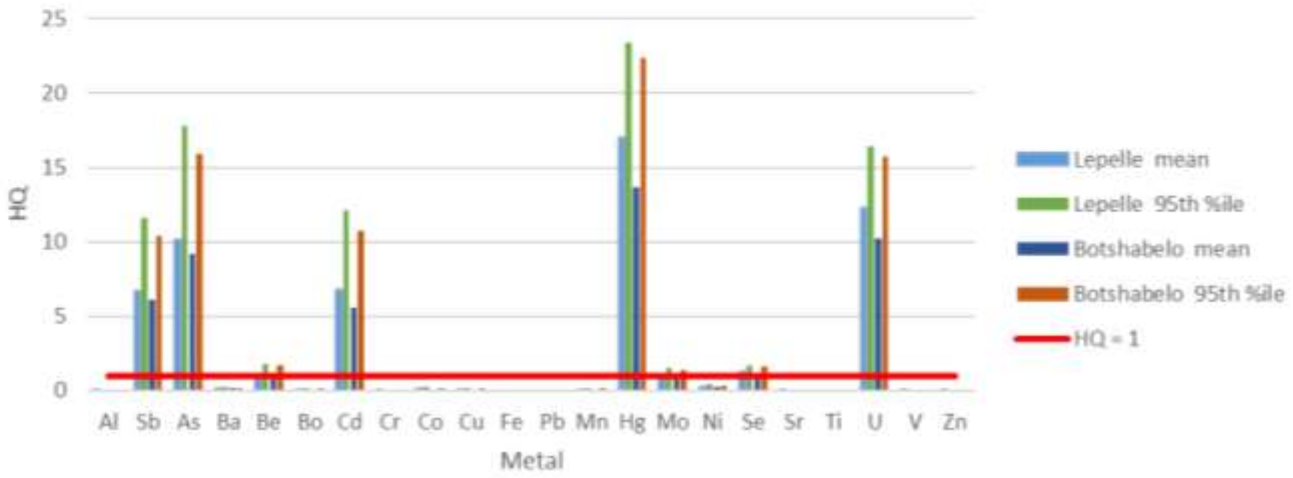

Fig. 3a. Hazard Quotients (non-carcinogenic risk) of metals/metalloids by ingestion of water in South Africa. HQ > 1 indicates a potential health risk and HQ < 1 indicates little or no significant potential health risks.

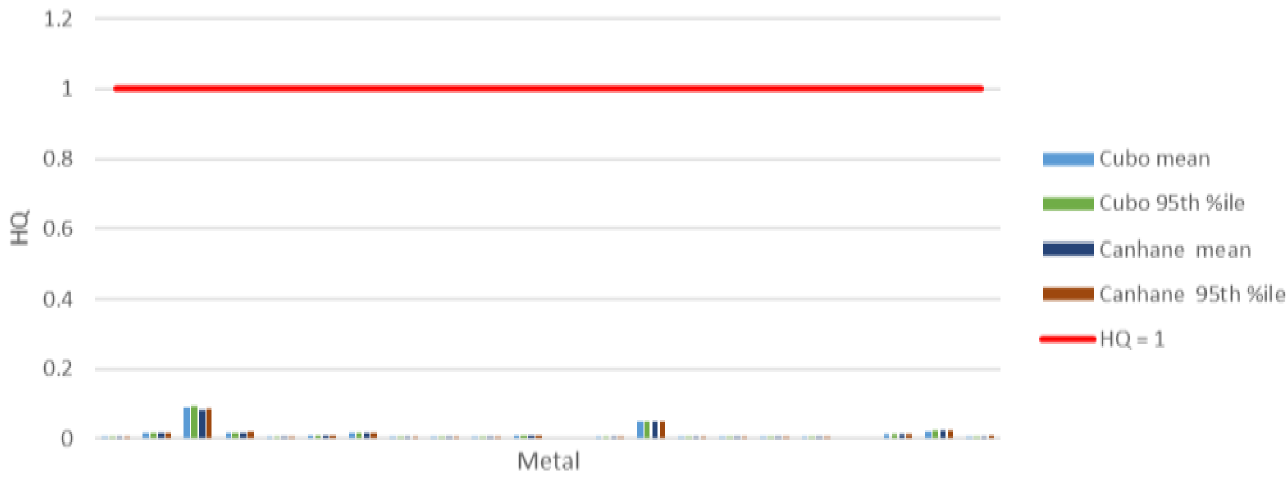

Fig. 3b. Hazard Quotients (non-carcinogenic risk) of metals/metalloids by ingestion of water in Mozambique. HQ > 1 indicates a potential health risk and HQ < 1 indicates little or no significant potential health risks.

3.6. Calculated non-carcinogenic vegetable health risks

The ADD values of metals/metalloids were calculated using the mean and 95th percentile of total concentrations of each metal in vegetable samples. Table S7 summarises the calculated ADD values for consumption of vegetable samples from sites in South Africa and Mozambique. The ADD values for aluminium, barium, mercury and uranium in vegetable samples from all sites in both countries were above their reference doses (an estimate of daily oral exposure to the human population that is unlikely to have detrimental effects during a lifetime). Vegetable samples from Lepelle, Botshabelo (South Africa) and Canhane (Mozambique) had ADD values for iron that were above the reference dose. The mean values for ADD of vegetable samples in South Africa increased in the following order: As < Cd < Mo < Pb < Co < Ni < Cr < V < U< Cu < B < Zn < Hg < Ba < Sr < Mn < Al < Fe. In Mozambique, vegetable samples' ADD values increased in the following order: Mo < Cd < Co < V < Cr < Ni < Pb < As < Cu < U < Ba < B < Zn < Sr < Mn < Hg < Al < Fe.

Non-carcinogenic health risks calculated as HQ values for vegetable samples from South African sites are presented in Figure 4a. The HQ for mean vegetable concentration was found to be greater than 1 for aluminium (Lepelle), arsenic (Botshabelo), barium (Lepelle), iron (Lepelle), uranium (Lepelle and Botshabelo) and vanadium (Lepelle).

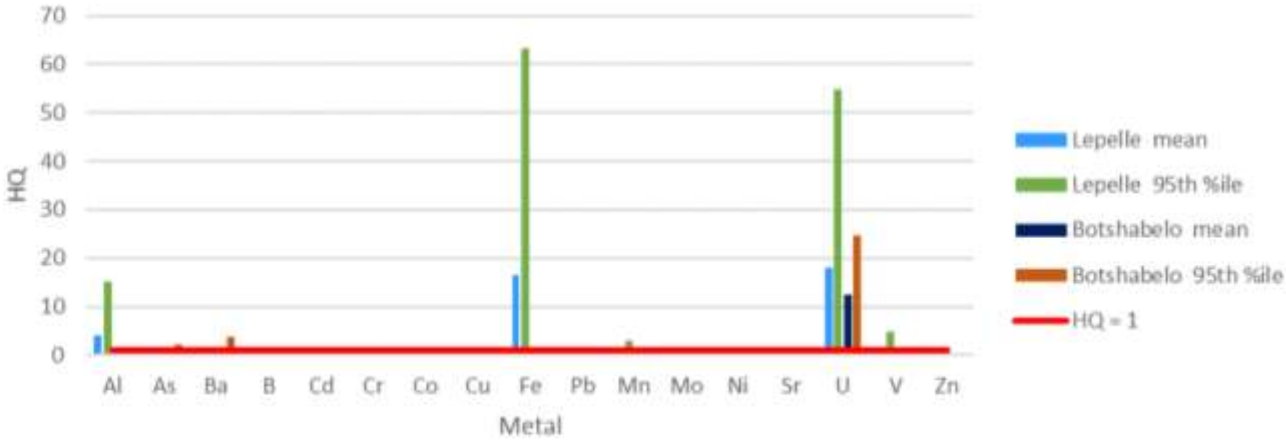

Fig. 4a. Hazard Quotients (non-carcinogenic risk) of metals/metalloids by ingestion of vegetables in South African sites.

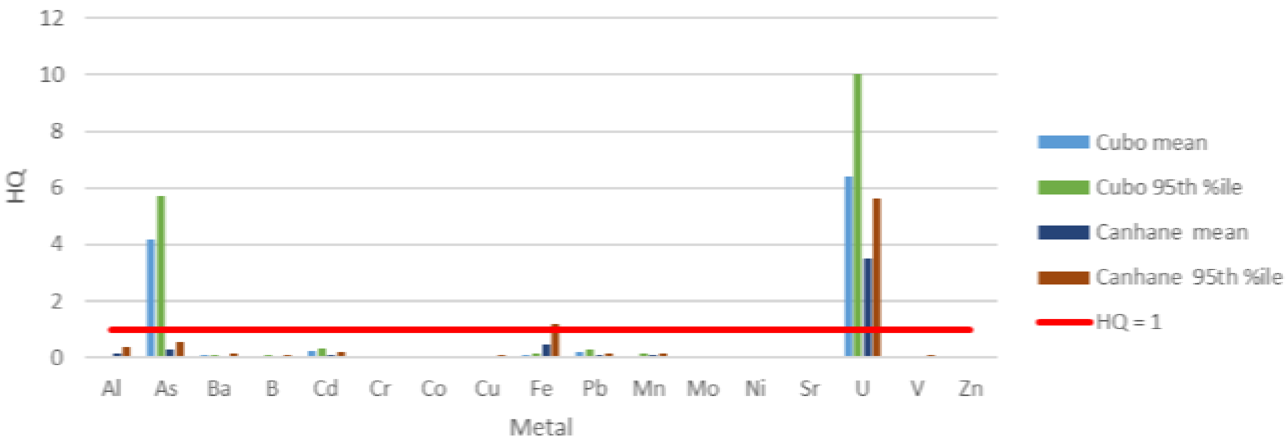

Fig. 4b. Hazard Quotients (non-carcinogenic risk) of metals/metalloids by ingestion of vegetables in Mozambican study sites.

HQ values for the Mozambican sites were greater than 1 for arsenic (Cubo), and uranium (Figure 4b). The HQ values for mercury across all sites were high, therefore they were omitted from the figures in order to show the detail of the smaller HQs. These values were 124.32 and 252.34 (Lepelle and Botshabelo, respectively) and 131.43 and 72. 38 (Cubo and Canhane, respectively).

3.7. Calculated carcinogenic water and vegetable health risks

Carcinogenic risk was assessed by calculating risk from LADD (Table 1). Nickel in water samples from Lepelle posed the highest carcinogenic risk based on the consumption of 2 litres of water per day. Arsenic in water samples posed the highest cancer risk in Botshabelo, Cubo and Canhane. Exposure to strontium from vegetable consumption had the highest carcinogenic risk in South African sites. The same was observed for sites in Mozambique.

Table 1. Theoretical excess cancer risk of metals/metalloids through water ingestion and vegetable consumption in South African (Lepelle and Botshabelo) and Mozambican (Cubo and Canhane) study sites.

		South Africa		**Mozambique**	
		Lepelle	**Botshabelo**	**Cubo**	**Canhane**
Water consumption	As	1.25E-05	1.14E-05	1.10E-07	1.02E-07
	Cr	3.59E-06	3.00E-06	2.61E-08	4.83E-08
	Pb	1.55E-11	1.66E-11	1.66E-10	1.66E-10
	Ni	2.04E-05	1.90E-05	2.57E-07	2.62E-07
	Sr	6.47E-06	5.37E-06	4.31E-06	4.34E-06
Vegetable consumption	As	7.05E-07	1.41E-06	5.17E-06	3.52E-07
	Cr	1.02E-05	4.70E-07	7.83E-08	1.02E-06
	Pb	1.69E-08	2.40E-08	1.46E-08	6.65E-09
	Ni	2.61E-05	8.14E-06	1.06E-06	2.93E-06
	Sr	4.80E-05	1.39E-04	1.88E-05	1.24E-05

4. Discussion

Heavy metal contamination of water, soil and vegetables has been investigated in mining areas (Bartrem et al., 2014; Bortey-Sam et al., 2015; Kamunda et al., 2016), urban areas (Ihedioha et al., 2014) and in coastal areas (Olawoyin et al., 2012). Some work has been done in African river systems (Jafarian-Dehkordi and Alehashem, 2013; Elumalai et al., 2017) including in our study area (Genthe et al., 2013). Ours is the first study to consider both water and vegetable heavy metal contamination in a human health risk assessment for two southern African country sites both considered to be affected by poor water quality in the Olifants

River. Our study also shows the effects of upstream as well as downstream impacts of observed anthropogenic sources.

The main findings were that metal concentrations in South Africa tended to be higher than those found in Mozambique, except for iron in water in Mozambique. The South African sites were closer to the source of the river, as well as to the ‘upstream’ industrial sites believed to be a primary source of pollution emission into the Olifants River. For the elevated levels of iron in water in Mozambique, a local source may influence this finding; similarly, for South African iron concentrations in vegetables which exceeded the World Health Organization limits other sources may exist. Known alternate pollutions sources include mining and related activities, mixed sources, fertiliser application, among others (Elulmalai et al., 2017).

In South Africa water samples with unsafe concentrations of antimony, arsenic, cadmium, chromium, mercury, molybdenum, nickel and selenium were found. These metals/metalloids have a range of impacts on human health (see Table S1), however, arsenic is one of most concern (Tchounwou et al., 2003). Arsenic was found in water samples from a South African study site, Botshabelo, at levels considered to be responsible for a 1 in 1000 chance of developing cancer based on the consumption of 2 litres of water per day. This is 100 times higher than the 1 in 100 000 acceptable risk as recommended by the World Health Organization. We also found non-carcinogenic vegetable risks of excess arsenic in both countries.

Excess cadmium exposure is associated with renal damage. In the Kempen region between Belgium and the Netherlands, there was an increased cadmium content of locally grown vegetables from air pollution, surface water pollution and solid waste build up and exposed individuals were found to have kidney malfunction (Kreis, 1990). The highest 24-hour urine cadmium levels were found in people who lived in areas that contained cadmium-polluted soils (Sartor et al., 1992). In one study, river water used to irrigate arable land was polluted with cadmium from tailings and wastewater of tungsten ore dressing plants (Cai et al., 1995). Cadmium concentrations in urine (11 µg/g creatinine), blood (12 µg/l) and in hair (0.11 µg/g) in people in the exposed area were sufficiently high to cause adverse renal effects in the long-term.

While mercury is not classifiable as a human carcinogen, chronic neurotoxic effects and damage to the nervous system, as well as renal disturbances, are among the non-carcinogenic health effects expected (ATSDR, 2017). These effects may be present among South Africans living in the two study sites where mercury in water and vegetables, was noted at levels that exceeded the World Health Organization guideline values. Mercury levels were also found to be high in the vegetable samples from Mozambique.

Non-carcinogenic risks from aluminium in vegetables South Africa sites were detected; adverse health effects of consuming plants high in aluminium include bone diseases and neurological disorders. The source of the aluminium may have been in part acidification of the soil from mining practices that result in acid mine draining. Accumulation of aluminium in the body with age may lead to apoptosis and immune suppression (Whiteside, 2006); this is a particular concern for exposed, vulnerable groups including the elderly and people with pre-existing diseases, especially HIV/AIDS.

The overall finding for the vegetables' metals/metalloids content and risk assessment was that uranium was between 10 and 20 times too high in SA and over 3 to 6 times in Mozambique if subsistence farming is being practiced. While uranium has not been classified in terms of it human carcinogenetic, intake of large concentrations can cause kidney disease (nephritis) and possible reproductive effects.

Nickel in water samples from Lepelle posed the highest carcinogenic risk based on the consumption of 2 litres of water per day. Nickel that is ingested orally may have limited intestinal absorption, however, chronic exposure is associated with cancer risk (Cempel and Nikel, 2005). Exposure to strontium from vegetable consumption had the highest carcinogenic risk in South African sites. The source of the strontium is not known, however, several studies have noted bioaccumulation of strontium in fish in the Olifants River (Avenant-Oldewage and Marx, 2000; Jordaan et al., 2016).

Finally, our findings confirm that less pollutants existed in the downstream sites in Mozambique suggesting that water quality improves to some extent as the water flows from areas where there are many stressors over many kilometres to end up in a neighbouring country where little to no stressors (apart from rural settlements) are present.

4.1. Study limitations

All human health risk assessments have inherent uncertainties. These range from uncertainties in the dose-response data used in the calculations to the environmental concentrations used in the dose (exposure) calculations. The study populations may also either be more, or less, exposed due to the assumptions used in the risk calculations. For instance, individuals in the study population may eat more than 240 g vegetables per day, or ingest more than the assumed 2 litres of water daily. This would result in higher than calculated risks. Similarly, if less is ingested than the assumptions made, the population would experience a lower incidence of adverse health effects. The timing of sample collection for the study was likely affected by season and additional samples, taken from different seasons may be required to supplement these findings.

5. Conclusions

Water and vegetable samples collected from two South African and two Mozambique sites were analysed for metals/metalloids and then findings were applied in a human health risk assessment to consider presence or absence of non-carcinogenic and carcinogenic health risks. When conducting such a study, it is important to consider all spheres to understand water quality and human health adverse health effects. We considered both water and vegetables, given that metals/metalloids in contaminated water via soil may bio-accumulate in plants prior to human consumption. Arsenic, mercury and uranium were the metals/metalloids presenting in the highest concentrations in both countries. Even with a reduction in the metal concentrations in water from South Africa to Mozambique, the potential to cause adverse human health impacts is still evident for both countries where indigent communities make direct use of untreated river water.

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References

Adriano, D.C., 2001. Trace Elements in Terrestrial Environments. Biogeochemistry, bioavailability and risks of metals. 2nd Ed. Springer-Verlag, New York. ISBN 0-387-98678-2. http://www.springer.com/gp/book/9780387986784

Amin, N., Hussain, A., Alamzeb, S., Begum, S., 2013. Accumulation of heavy metals in edible parts of vegetables irrigated with waste water and their daily intake to adults and children, District Mardan, Pakistan. Food Chem 136(3), 1515-1523. DOI: https://doi.org/10.1016/j.foodchem.2012.09.058

APHA, 2017. Standard methods for the examination of water and wastewater – 23rd edition. American Public Health Association. http://www.standardmethods.org/

ATSDR, 2017. Agency for Toxic Substances and Disease Registry. https://www.atsdr.cdc.gov/index.html.

Avenant-Oldewage, A., Marx, H., 2000 Manganese, nickel and strontium bioaccummulation in the tissues of the African sharptooth catfish, Clarias gariepinus from the Olifants River, Kruger National Park. Koedoe 2,17-33. DOI: 10.4102/koedoe.v43i2.196.

Bartrem, C., Tirima, S., von Lindern, I., von Braun, M., Worrell, M.C., Mohammad Anka, S., Abdullahi, A., Moller, G., 2014. Unknown risk: co-exposure to lead and other heavy metals among children living in small-scale mining communities in Zamafara State, Nigeria. Int J Environ Health Res 24(4), 304-319. DOI: 10.1080/09603123.2013.835028.

Bortey-Sam, N., Nakayama, S.M., Ikenaka, Y., Akoto, O., Baidoo, E., Mizukawa, H., Ishizuka, M., 2015. Health risk assessment of heavy meatals and mettaloid in drinking water from communities near gold mines in Tarkwa, Ghana. Environ Monit Assess 187(77), 397. DOI: 10.1007/s10661-015-4630-3.

Cai, S., Yue, L., Shang, Q. and Nordberg, G., 1995. Cadmium exposure among residents in an area contaminated by irrigation water in China. Bull World Health Organ 73(3), 359-367. PMCID: PMC2486658.

Cempel, M., Nikel, G., 2006. Nickel: A rview of its sources and environmental toxicology. Polish J of Enviorn Stud 15(3), 375-382.

Chaney, R.L., Li, Y-M., Brown S.L., Homer, F.A., Malik, M., Angle, J.S., Baker, A.J.M, Reeves, R.D., Chin, M., 1999. Improving metal hyperaccumulator wild plants to develop commercial phytoextraction systems. In Phytoremediation of Contaminated Soil and Water, Chapter 7, CRC Press. http://www.crcnetbase.com/doi/abs/10.1201/9781439822654.ch7

Dabrowski, J.M., Ashton, P.J., Murray, K., Leaner, J.J., Mason, R.P., 2008. Anthropogenic mercury emissions in South Africa: Coal combustion in power plants. Atmospheric Environment 42(27), 6620-6626. https://doi.org/10.1016/j.atmosenv.2008.04.032

DEA, 2010. The Framework for the Management of Contaminated Land. Department of Environmental Affairs, Pretoria, South Africa.

DWA, 2011. Green Drop Report 2010. South African Waste Water Quality Management Performance. Department of Water Affairs, Pretoria, South Africa.

Elumalai, V., Brindha, K., Lakshmanan, E., 2017. Human exposure risk assessment due to heavy meatsls in groundwater by pollution index and multivariate statistical methods: a case study from South Africa. Water 9, 234. DOI: 10.3390/w9040234

Genthe, B., Le Roux, W.J., Schachtschneider, K., Oberholster, P.J., Aneck-Hahn, N.H., Chamier, J., 2014. Health risk implications from simultaneous exposure to multiple environmental contaminants. Ecotoxicol Environ Saf 93,171-179. DOI: 10.1016/j.ecoenv.2013.03.032

Grobler, D., Kempster, P.L., van der Merwe, L., 1994. A note on the occurrence of metals in the Olifants River, Eastern Transvaal, South Africa. Water SA 20(3), 195-204. http://www.wrc.org.za/Knowledge%20Hub%20Documents/Water%20SA%20Journals/Manuscripts/1994/03/WaterSA_1994_03_0787.PDF

Gupta, U.C., Gupta, S.C., 1998. Trace element toxicity relationships to crop production and livestock and human health: implications for management. Commun Soil Sci Plant Anal 29, 1491–522. DOI: http://dx.doi.org/10.1080/00103629809370045

Hobbs, P., Oelofse, S.H.H., Rascher, J., 2008. Management of environmental impacts from coal mining in the upper Olifants River catchment as a function of age and scale. Int J Water Res Dev 24(3), 417-431. DOI: http://dx/doi.org/10.1080/07900620802127366

Hunter, P.R., Macdonald, A.M., Carter, R.C., 2010. Water supply and health. PLoS Med, 7(11): e1000361. DOI: https://doi.org/10.1371/journal.pmed.1000361

Ihedioha JN, Okoye CO and Onyechi UA. Health risk assessment of zinc, chromium and nickel from cow meat consumption in an urban Nigerian population. Int J Occup Environ Health 2014; 20(4): 281-288. DOI: 10.1179/2049396714Y.0000000075

Jafarian-Dehkordi, A., Alehashem, M., 2013 Heavy metal contamination of vegetables in Isfahan, Iran. Res Pharm Sc 8(1), 51-58. PMCID: PMC3895300

Jordaan, L.J., Wepener, V., Huizenga, J.M., 2016. The strontium isotope distribution in water and fish within major South African catchments. Water SA 42(2), 213-224. https://www.ajol.info/index.php/wsa/article/view/138069

Kamunda, C., Mathuthu, M., Madhuku, M., 2016. Health risk assessment of heavy metals in soils from Witwatersrand gold mining basin, South Africa. Int J Env Res and Pub Health 13: 663. DOI: 10.3390/ijerph13070663

Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z. and Zhu, Y.G., 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ Poll 152(3), 686-692. DOI: 10.1016/j.envpol.2007.06.056

Kreis, I.A., 1990. Cadmium contamination of the countryside, a case study on health effects. Toxicol Ind Health 6(5), 181-189. https://www.ncbi.nlm.nih.gov/labs/articles/2274982/

McBride, M.B., 2007. Trace metals and sulphur in soils and forage of a chronic wasting disease. Environ Chem 4, 134–139. DOI: https://doi.org/10.1071/EN06066

McLaughlin, M.J., Parker, D.R, Clarke, J.M., 1999. Metals and micronutrients-food safety issues. Field Crops Res 60, 143–63. DOI: https://doi.org/10.1016/S0378-4290(98)00137-3

Monika, D.P., Katarzyna, S.K., 2004. Histopathological changes in the liver, kidneys, and testes of bank voles environmentally exposed to heavy metal emissions from the steelworks and zinc smelter in Poland. Environ Res 96, 72–78. DOI: 10.1016/j.envres.2004.02.003

Oberholster, P.A.H., Ashton, P.J., Both, A.M. et al. (2010). Risk Assessment of Pollution in Surface Waters of the Upper Olifants River System: Implications for Aquatic Ecosystem Health and the Health of Human Users of Water. CSIR Report No. CSIR/NRE/WR/IR/2011/0041/B. Council for Scientific and Industrial Research, Pretoria, South Africa. Available from bgethe@csir.co.za

Olawoyin, R., Oyewole, S.A., Grayson, R.L., 2012. Potenbtial risk effect from elevated leels of soil heavy metals on human health in the Niger delta. Ecotoxicol Environ Saf 85, 120-130. DOI: 10.1015/j.ecoenv.2012.08.004

Pruvot, C., Douay, F., Hervé, F., Waterlot, C., 2006. Heavy Metals in Soil, Crops and Grass as a Source of Human Exposure in the Former Mining Areas. J Soils Sediments 6 (4) 215-220. DOI: 10.1065/jss2006.10.186

Sartor, F.A., Rondia, D.J., Claeys, F.D., Staessen, J.A., Lauwerys, R.R., Bernard, A.M., Buchet, J.P., Roels, H.A., Bruaux, P.J., Ducoffre, G.M. et al., 1992. Impact of environmental cadmium pollution on cadmium exposure and body burden. Arch Environ Health 47(5), 347-353. DOI: http://dx.doi.org/10.1080/00039896.1992.9938373

Sipter, E., Rozsa, E., Gruiz, K., Tatrai, E., Morvai, V., 2008. Site-specific risk assessment in contaminated vegetable gardens. Chemosphere 71(7), 1301-1307. DOI: https:doi.org/10.1016/j.chemosphere.2007.11.039

StataCorp, 2015. Stata Statistical Software Release 14, College Station, Texas, StataCorp, LP.

Tchounwou, P.B., Patlolla, A.K., Centeno, J.A., 2003. Carcinogenic and systematic health effects associated with arsenic exposure – a critical review. Toxicologic Pathology 31(6), 575-588. http://journals.sagepub.com/doi/abs/10.1080/01926230390242007

USEPA, 1992. Guidelines for Exposure Assessment. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC EPA/600/Z-92/001. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=15263

USEPA, 1999. Guidance for Performing Aggregate Exposure and Risk Assessments. U.S. Environmental Protection Agency, Office of Pesticide Programs, Washington DC. https://archive.epa.gov/scipoly/sap/meetings/web/pdf/guidance.pdf

USEPA, 2000. Integrated Risk Information System (IRIS) Database. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. https://www.epa.gov/iris

USEPA, 2011. Exposure Factors Handbook: 2011 Edition. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC 20460, National Center for Environmental Assessment. EPA/600/R-090/052F, September 2011.

USEPA, 2012. U.S. EPA (U.S. Environmental Protection Agency). 2012. Human Health Risk Assessment. http://www.epa.gov/risk/health-risk.htm

USEPA, 2013. U.S. EPA (U.S. Environmental Protection Agency). 2013. Surface Water Sampling (SESDPROC-201-R3). https://www.epa.gov/sites/production/files/2015-06/documents/Surfacewater-Sampling.pdf

USEPA, 2015. RSL Calculator [Online]. http://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search

Whiteside, T.L., 2006. Immune suppression in cancer: effects on immune cells, mechanisms and future therapeutic intervention. Semin Cancer Biol 19(1), 3-15. DOI: 10.1016/j.semcancer.2005.07.008

WHO, 2003. Iron in drinking-water. Background document for development of WHO Guidelines for drinking-water quality. World Health Organization, Geneva, Switzerland. http://www.who.int/water_sanitation_health/dwq/chemicals/iron.pdf

WHO, 2004. The Global Burden of Disease Report. World Health Organization, Geneva, Switzerland. http://www.who.int/topics/global_burden_of_disease/en/

WHO, 2008. Guidelines for drinking-water quality. World Health Organization, Geneva, Switzerland. http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/

Supplementary tables and figures

Table S1. Summary of documented health effects of contaminants found at higher than recommended levels in environmental water and vegetable samples (Source ATSDR).

Contaminant of potential concern	**Documented health effects**	
	Toxic effects	**Carcinogenic effects**
Aluminium (Al)	Suspected causal link to Alzheimer's but weight of evidence inconclusive; neurological effects and dementia in patients with renal failure and those receiving dialysis (dialysis encephalopathy).	Class D: Not classifiable as to human carcinogenicity
Antimony (Sb)	Antimony effects observed in animal studies showed life spans to be significantly reduced i.e. decreased longevity, as well as disturbances in glucose and cholesterol metabolism being observed in rats. Seventy people became acutely ill after drinking lemonade containing 0.013% antimony. A reference dose of 0.0004mg/kg bw/day was developed making use of animal data.	
Arsenic (As)	Chronic effects: skin lesions and hyper-pigmentation. Arsenic can accumulate in the body. Acute effects: death from upper respiratory, pulmonary, gastrointestinal and cardiovascular failure. Nerve damage and sensory loss in the peripheral nervous system is a primary symptom of arsenic poisoning. Skin contact with inorganic arsenic may cause redness and swelling.	**Class A: Known human carcinogen.** Causes cancer of the skin and internal organs.
Cadmium (Cd)	Severe renal damage and renal failure, acute gastroenteritis.	Class B1: Probable human carcinogen - based on limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in animals.
Chromium (Cr)	Stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain Cr(VI) compounds can cause skin ulcers. Inhalation of Cr(VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum.	Class D: Not classifiable as human carcinogen via oral route Class A: Human carcinogen via inhalation route. Cr(VI) compounds can increase the risk of lung cancer.
Cobalt (Co)	Serious effects on the heart and in extreme cases death. Nausea and vomiting are usually reported before the effects on the heart are noticed. Longer-term exposure of rats, mice, and guinea pigs to lower levels of cobalt in the food or drinking water results in effects on heart, liver, kidneys, and blood as well as the testes, and also causes effects on behaviour.	The International Agency for Research on Cancer (IARC) has listed cobalt as possibly carcinogenic to humans

Copper (cu)	Ingestion of copper may cause nausea, vomiting, stomach cramps, or diarrhoea. Intentionally high intakes of copper can cause liver and kidney damage and even death.	Class D: Not classifiable as to human carcinogenicity
Iron (Fe)	The toxic effects of ingesting high levels of iron result from massive iron overload in the tissues (haemochromatosis) and cirrhosis of the liver. The US EPA provisional reference dose (RfD) for iron is the no observable adverse effect level (NOAEL) in humans of 0.3 mg/kg/day.	Not suspected to be carcinogenic.
Manganese (Mn)	Neurotoxic effects may result from extreme exposure. Uptake is greater from food than water. . Exposure to excess manganese may cause Parkinson-like symptoms, infertility in mammals and malfunction of the immune system	Class D: Not classifiable as to human carcinogenicity.
Mercury (Hg)	Chronic neurotoxic effects, damage to nervous system. Neurological (organic Hg) and renal disturbances (inorganic Hg). Organically-bound Hg is more toxic than inorganic. Elemental Hg is volatile and exposure by inhalation may also occur.	Class D: Not classifiable as to human carcinogenicity.
Nickel (Ni)	Decreased body and organ weights in animals.	Class A: Known human carcinogen.
Uranium (U)	Radioactive substance, intake of large concentrations can cause kidney disease (nephritis), possible reproductive effects	Group V: inadequate data for evaluation of carcinogenicity.
Vanadium (V)	Ingesting vanadium can cause nausea and vomiting and mild neurological effects. In animals, ingesting vanadium has been found to cause decreased red blood cells and increased blood pressure. Long-term oral exposure of rats to vanadium causes minor cell changes in the kidney and lungs. Female rats exposed to vanadium have offspring of decreased body weights. It is unknown whether humans experience effects similar to vanadium-exposed rats. The oral RfD for vanadium is currently under review by the US EPA. The provisional oral RfD for vanadium, 0.001 mg/kg-day, is based on a study in which rats were administered vanadium in their drinking water.	EPA has not classified vanadium as to its human carcinogenicity.
Zinc (Zn)	Although zinc is an essential element, as excess amount can cause gastrointestinal disturbances, nausea and vomiting.	Class D: Not classifiable as to human carcinogenicity.

Table S2. Cancer slope factors (*CSF*) for metals/metalloids.

Heavy Metal	Oral RfD (mg/kg-d)	Oral CSF	Reference
Aluminium (Al)	1	1.5	(DEA, 2010)
Arsenic (As)	0.0003	*	(USEPA, 2000)
Boron (B)	0.09	*	(CSIR, 2014)
Barium (Ba)	7.0E-02	*	(USEPA, 2000)
Beryllium (Be)	2.0E-03	*	(USEPA, 2000)
Cadmium (Cd)	1.0E-03 (food) 5.0E-04 (water)	*	(USEPA, 2000)
Cobalt (Co)	0.02	*	(USEPA, 2002)
Chromium (Cr)	3.0E-03 (Cr VI) 1.5E+00 (Cr III)	0.5	(USEPA, 2000; DEA, 2010; USEPA 2015)
Copper (Cu)	0.04	*	(DEA, 2010)
Iron (Fe)	0.3	*	(CSIR, 2014)
Mercury (Hg)	0.0003	*	(USEPA, 2000)
Manganese (Mn)	0.14 (food) 0.046 (water)	*	(USEPA, 2000)
Molybdenum (Mo)	0.005	*	(USEPA, 2000)
Nickel (Ni)	0.02	1.7	(USEPA, 2000; USEPA 2015)
Lead (Pb)	0.0036	0.0085	(DEA, 2010)
Antimony (Sb)	0.0004	*	(USEPA, 1992)
Selenium (Se)	5.0E-03	*	(CSIR, 2014)
Strontium (Sr)	0.6	0.5	(USEPA, 1992; USEPA 2015)
Uranium (U)	0.0006	*	(CSIR, 2014)

Vanadium (V)	0.009	*	(USEPA, 2000)
Zinc (Zn)	0.3	*	(USEPA, 2000)

Note. * denotes no oral CSF exists for specific metals.

Table S3. Mean metal/metalloid concentrations for water (µg/L) and vegetable (mg/kg) samples in all samples and by country.

	Water			Vegetables		
	Mean both countries (µg/L)	**Mean South Africa (µg/L)**	**Mean Mozambique (µg/L)**	**Mean both countries (mg/kg)**	**Mean South Africa (mg/kg)**	**Mean Mozambique (mg/kg)**
Aluminium (Al)	**207.33**	**278.42**	115.93	**497.26**	**798.21**	29.11
Antimony (Sb)	51.38	91.14	0.25	N/A	N/A	N/A
Arsenic (As)	58.52	103.07	1.24	0.10	0.07	0.14
Barium (Ba)	**212.71**	**349.03**	37.43	10.15	15.86	1.28
Beryllium (Be)	39.65	70.29	0.25	BDL	BDL	BDL
Boron (B)	**207.11**	**313.74**	70.00	2.78	3.71	1.33
Cadmium (Cd)	62.55	111.01	0.25	0.06	0.17	0.04
Chromium (Cr)	49.12	86.67	0.85	0.93	1.43	0.15
Cobalt (Co)	44.25	78.48	0.25	0.32	0.48	0.06
Copper (Cu)	55.09	94.83	4.00	2.24	3.37	0.48
Iron (Fe)	33.08	0.03	**75.57**	**596.17**	**960.57**	29.33
Lead (Pb)	0.14	0.02	0.29	0.19	0.24	0.12
Manganese (Mn)	71.38	126.23	0.86	18.15	27.60	3.44
Mercury (Hg)	94.21	167.10	0.50	12.21	14.88	8.06
Molybdenum (Mo)	78.28	138.17	1.29	BDL	BDL	BDL
Nickel (Ni)	85.21	150.03	1.86	0.81	1.23	0.14
Selenium (Se)	116.92	**207.82**	0.05	BDL	BDL	BDL
Strontium (Sr)	148.79	155.96	139.57	11.66	17.16	3.10
Titanium (Ti)	**236.87**	**418.16**	3.79	N/A	N/A	N/A

Uranium (U)	137.04	**243.12**	0.66	2.02	2.82	0.78
Vanadium (V)	5.35	0.03	12.20	1.33	2.13	0.79
Zinc (Zn)	**216.29**	**370.07**	18.57	9.60	14.05	2.67

Note. N/A, not available. BDL, below detection limit. BDL for Beryllium was 0.02, molybdenum was 0.7 and Selenium was 8.8.

Table S4. World Health Organisation drinking water guideline values (WHO, 2008) and recommended maximum levels in vegetables (WHO, 2001).

	Water	Vegetables
	Guideline value * (ug/L)	**Guidelines value (mg/kg)**
Antimony (Sb)	20.0	-
Arsenic (As)	10.0	-
Barium (Ba)	700.0	-
Boron (B)	500.0	-
Cadmium (Cd)	3.0	0.3
Chromium (Cr)	50.0	5.0
Copper (Cu)	2000.0	40.0
Iron (Fe)	9.0	450.0
Lead (Pb)	10.0	5.0
Manganese (Mn)	500.0	-
Mercury (Hg)	6.0	-
Molybdenum (Mo)	70.0	-
Nickel (Ni)	20.0	20.0
Selenium (Se)	10.0	-
Uranium (U)	15.0	-
Zinc (Zn)	3000.0	60.0

*Safe level for intake.

Table S5. Analysis of variance of metals/metalloids in water and vegetables samples in South Africa and Mozambique. Results with statistically significant *p values* are highlighted in bold.

	Water samples		**Vegetable samples**	
	F	*P value*	*F*	*P value*
Al	8.6	0.0109	2.25	0.1486
Sb	17.74	0.0009	*	*
As	**16.62**	**0.0011**	1.54	0.2283
Ba	**22.72**	**0.0003**	3.04	0.0959
Be	15.09	0.0017	*	*
B	**11.62**	**0.0042**	3.38	0.0801
Cd	**13.18**	**0.0027**	2.3	0.1441
Cr	**14.35**	**0.002**	1.76	0.1993
Co	**14.79**	**0.0018**	1.56	0.2259
Cu	**13.24**	**0.0027**	5.38	0.0305
Fe	**67.93**	**<0.000**	2.08	0.1645
Pb	**70.42**	**<0.000**	2.56	0.1242
Mn	**15.2**	**0.0016**	2.83	0.1074
Hg	**20.18**	**0.0005**	3.53	0.0743
Mo	**14.77**	**0.0018**	1.37	0.255
Ni	**14.38**	**0.002**	2.18	0.1551
Se	**27.57**	**0.0001**	*	*
Sr	0.1	0.7577	1.71	0.2046
Ti	27.34	0.0001	*	*
U	**27.79**	**0.0001**	4	0.0585
V	**6.49**	**0.0232**	1.93	0.1796
Zn	**17.93**	**0.0008**	7.25	0.0136

Note. * denotes that samples were not analysed for that metal or the concentration was below the detection limit

Table S6. Average Daily Dose of metals/metalloids by ingestion of water (mg/kg/day).

	South African sites				**Mozambican sites**			
	Lepelle		**Botshabelo**		**Cubo**		**Canhane**	
	Mean	**95th percentile**	**Mean**	**95th percentile**	**Mean**	**95th percentile**	**Mean**	**95th percentile**
Al	8.42E-03	1.13E-02	7.03E-03	1.08E-02	4.08E-03	4.59E-03	3.63E-03	4.41E-03
Sb	**2.69E-03***	**4.63E-03***	**2.43E-03***	**4.15E-03***	7.14E-06	7.14E-06	7.14E-06	7.14E-06
As	**3.03E-03***	**5.34E-03***	**2.77E-03***	**4.76E-03***	2.67E-05	2.83E-05	2.48E-05	2.57E-05
Ba	1.05E-02	1.41E-02	8.82E-03	1.35E-02	1.11E-03	1.22E-03	1.23E-03	1.26E-03
Be	**2.12E-03***	**3.60E-03***	1.78E-03	**3.34E-03***	7.14E-06	7.14E-06	7.14E-06	7.14E-06
B	9.48E-03	1.27E-02	7.92E-03	1.22E-02	6.57E-04	7.09E-04	6.86E-04	8.09E-04
Cd	**3.37E-03***	**6.04E-03***	**2.77E-03***	**5.38E-03***	7.14E-06	7.14E-06	7.14E-06	7.14E-06
Cr	2.62E-03	4.50E-03	2.19E-03	4.17E-03	1.90E-05	2.00E-05	3.52E-05	5.89E-05
Co	2.37E-03	4.05E-03	1.99E-03	3.76E-03	7.14E-06	7.14E-06	7.14E-06	7.14E-06
Cu	2.86E-03	4.95E-03	2.40E-03	4.58E-03	9.52E-05	1.11E-04	9.52E-05	1.11E-04
Fe	7.14E-07	7.14E-07	7.14E-07	7.14E-07	2.72E-03	2.84E-03	2.10E-03	2.59E-03
Pb	6.67E-07	7.14E-07	7.14E-07	7.14E-07	7.14E-06	7.14E-06	7.14E-06	7.14E-06
Mn	3.71E-03	6.75E-03	3.40E-03	5.99E-03	2.76E-05	3.34E-05	2.76E-05	2.86E-05
Hg	**5.11E-03***	**7.02E-03***	**4.11E-03***	**6.71E-03***	1.43E-05	1.43E-05	1.43E-05	1.43E-05
Mo	4.05E-03	**7.45E-03***	3.74E-03	**6.61E-03***	1.43E-05	1.43E-05	1.43E-05	1.43E-05
Ni	4.39E-03	8.16E-03	4.09E-03	7.22E-03	5.52E-05	5.71E-05	5.62E-05	6.20E-05
Se	**6.29E-03***	**8.45E-03***	**5.24E-03***	**8.07E-03***	1.43E-06	1.43E-06	1.43E-06	1.43E-06
Sr	4.73E-03	8.86E-03	3.92E-03	7.83E-03	3.14E-03	3.19E-03	3.17E-03	3.20E-03
Ti	1.26E-02	1.70E-02	1.05E-02	1.62E-02	1.24E-04	1.40E-04	1.24E-04	1.40E-04
U	**7.35E-03***	**9.87E-03***	**6.13E-03***	**9.43E-03***	7.14E-06	7.14E-06	7.14E-06	7.14E-06
V	8.57E-07	1.36E-06	7.14E-07	7.14E-07	1.88E-04	2.05E-04	1.97E-04	2.14E-04
Zn	1.13E-02	1.56E-02	9.10E-03	1.49E-02	2.95E-04	7.49E-04	9.33E-04	2.47E-03

Table S7. Average Daily Dose of metals/metalloids by consumption of vegetables (mg/kg/day) in South Africa (Lepelle and Botshabelo) and Mozambique (Cubo and Canhane).

	South African sites				Mozambican sites			
	Lepelle		Botshabelo		Cubo		Canhane	
	Mean	95th percentile	Mean	95th percentile	Mean	95th percentile	Mean	95th percentile
Al	**4.08E+00***	**1.52E+01***	**3.11E-01***	**6.39E-01***	**2.29E-02***	**3.67E-02***	**1.38E-01***	**3.82E-01***
As	1.71E-04	2.74E-04	3.43E-04	6.51E-04	1.26E-03	1.71E-03	8.57E-05	1.71E-04
Ba	**4.19E-02***	**1.17E-01***	**7.68E-02***	**2.63E-01***	**5.71E-03***	**6.86E-03***	**3.71E-03***	**9.43E-03***
B	1.10E-02	2.74E-02	1.58E-02	3.36E-02	5.71E-03	9.94E-03	4.00E-03	9.43E-03
Cd	1.71E-04	2.74E-04	3.43E-04	6.51E-04	2.29E-04	3.26E-04	8.57E-05	1.71E-04
Cr	**7.43E-03***	**2.83E-02***	3.43E-04	6.86E-04	5.71E-05	1.54E-04	7.43E-04	2.06E-03
Co	2.38E-03	9.67E-03	3.43E-04	6.51E-04	2.29E-04	3.26E-04	2.00E-04	3.43E-04
Cu	1.38E-02	**4.00E-02***	7.47E-03	1.26E-02	6.86E-04	1.27E-03	2.11E-03	3.26E-03
Fe	**4.99E+00***	**1.90E+01***	2.39E-01	**4.61E-01***	2.74E-02	4.29E-02	1.37E-01	**3.57E-01***
Pb	7.24E-04	2.06E-03	1.03E-03	2.06E-03	6.29E-04	9.77E-04	2.86E-04	4.71E-04
Mn	1.37E-01	**4.42E-01***	1.89E-02	3.11E-02	1.05E-02	2.19E-02	1.25E-02	2.16E-02
Hg	**3.73E-02***	**6.50E-02***	**7.57E-02***	**1.38E-01***	**3.94E-02***	**6.19E-02***	**2.17E-02***	**3.47E-02***
Mo	0.00E+00	0.00E+00	6.86E-04	1.71E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Ni	5.60E-03	**2.13E-02***	1.75E-03	4.32E-03	2.29E-04	3.26E-04	6.29E-04	1.29E-03
Sr	3.50E-02	1.23E-01	1.02E-01	3.40E-01	1.37E-02	1.69E-02	9.09E-03	1.80E-02
U	**1.09E-02***	**3.29E-02***	**7.54E-03***	**1.47E-02***	**3.83E-03***	**6.02E-03***	**2.09E-03***	**3.39E-03***
V	**1.11E-02***	**4.29E-02***	4.46E-04	6.86E-04	2.29E-04	3.26E-04	3.71E-04	9.43E-04
Zn	4.85E-02	1.17E-01	4.76E-02	9.94E-02	1.07E-02	1.56E-02	8.34E-03	1.37E-02

Note. *above RfD

Supplementary Figures

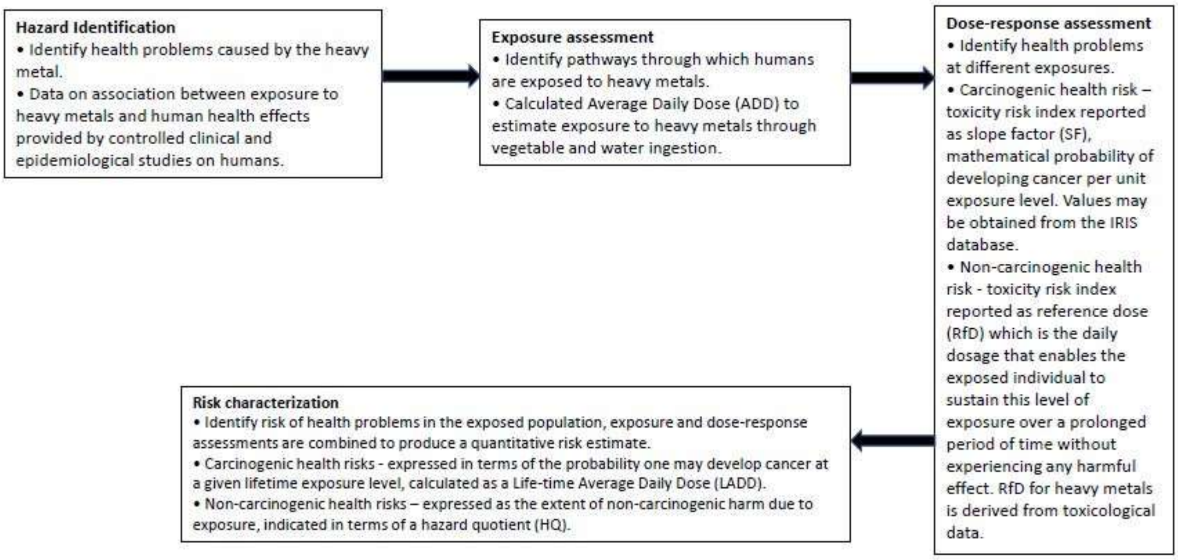
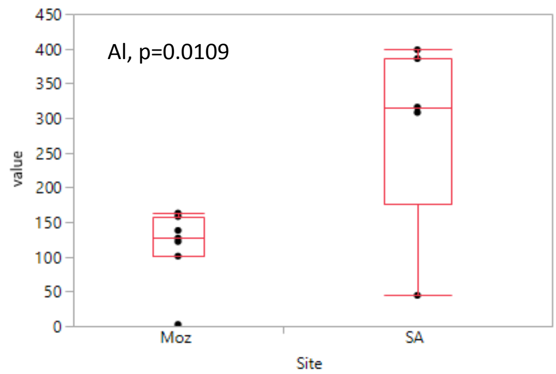


Figure S1. Human Health Risk Assessment Model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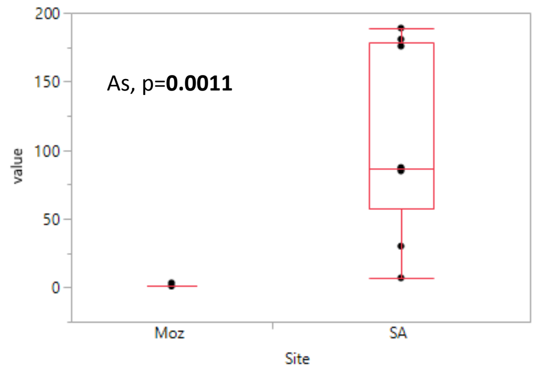
300
250
200
150
100
50
0
value
Moz
SA
Site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0
value
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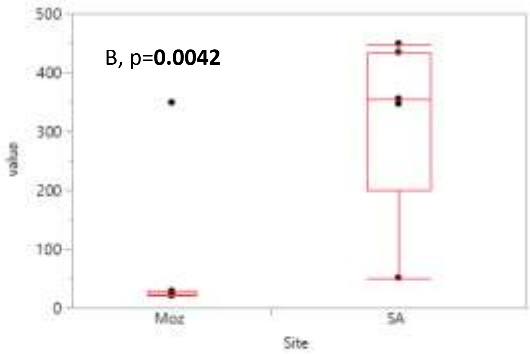
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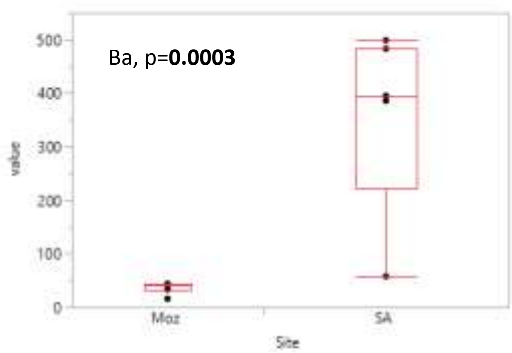
100
0
value
Moz
SA
Site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200
100
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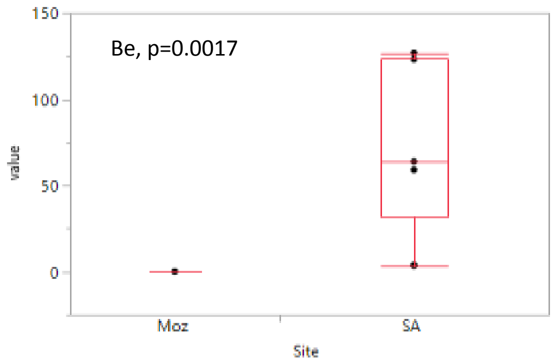
value
Moz
SA
Site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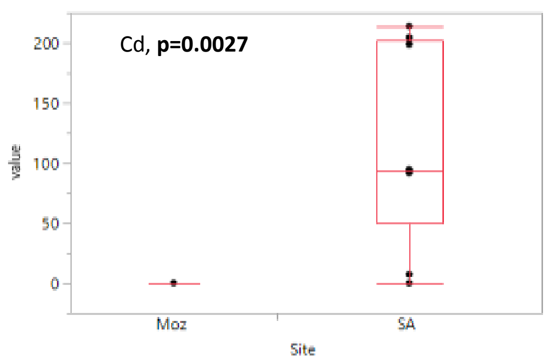
100
50
0
value
Moz
SA
Site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150
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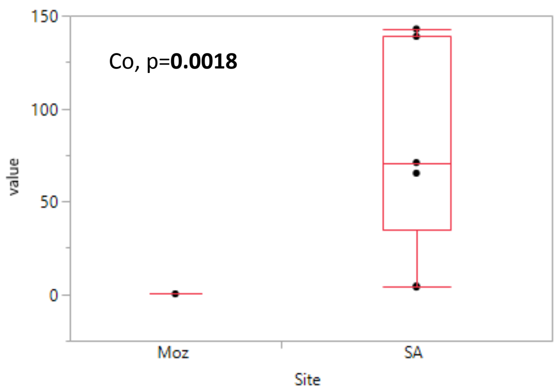
50
0
value
Moz
SA
Site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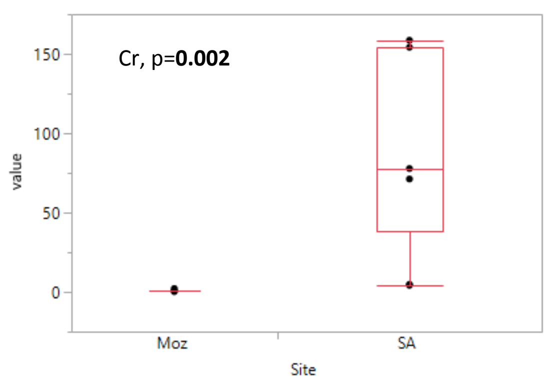
100
50
0
value
Moz
SA
Site


Cr, p=**0.002**
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100
50
0
value
Moz
SA
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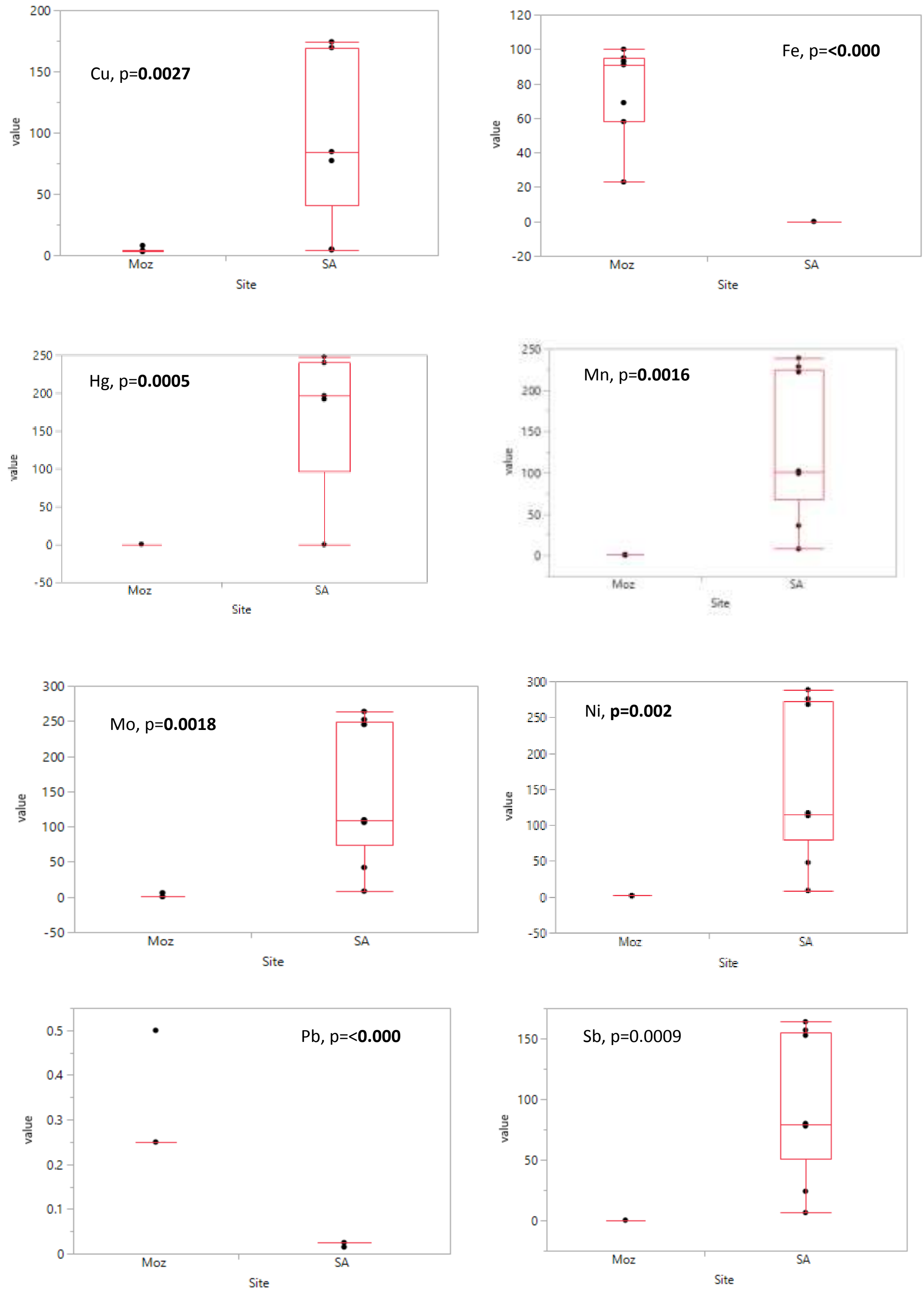
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Fe, p=**<0.000**
Hg, p=**0.0005**
Mn, p=**0.0016**
Mo, p=**0.0018**
Ni, **p=0.002**
Pb, p=<**0.000**
Sb, p=0.0009
value
Site
Moz
SA

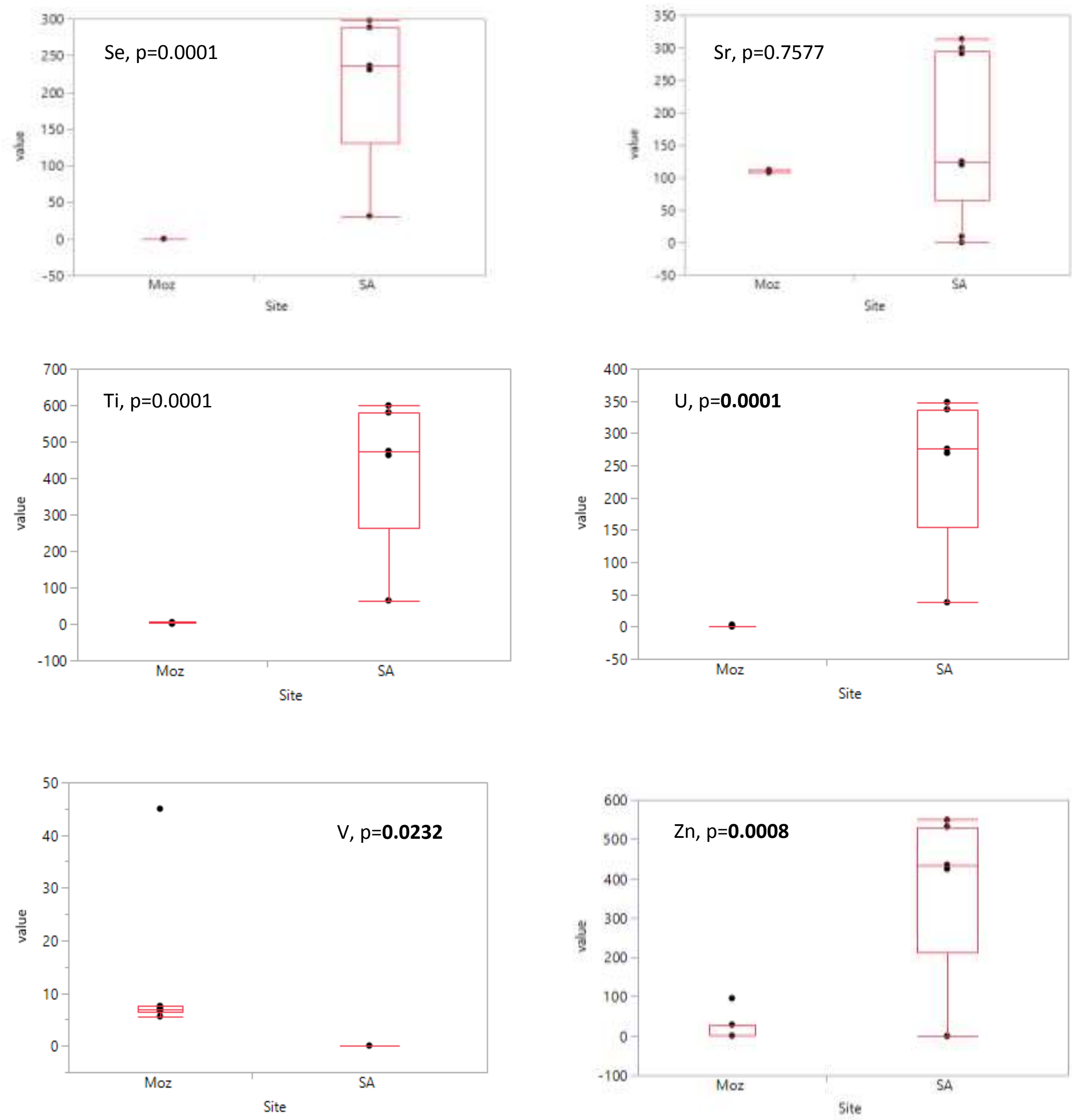
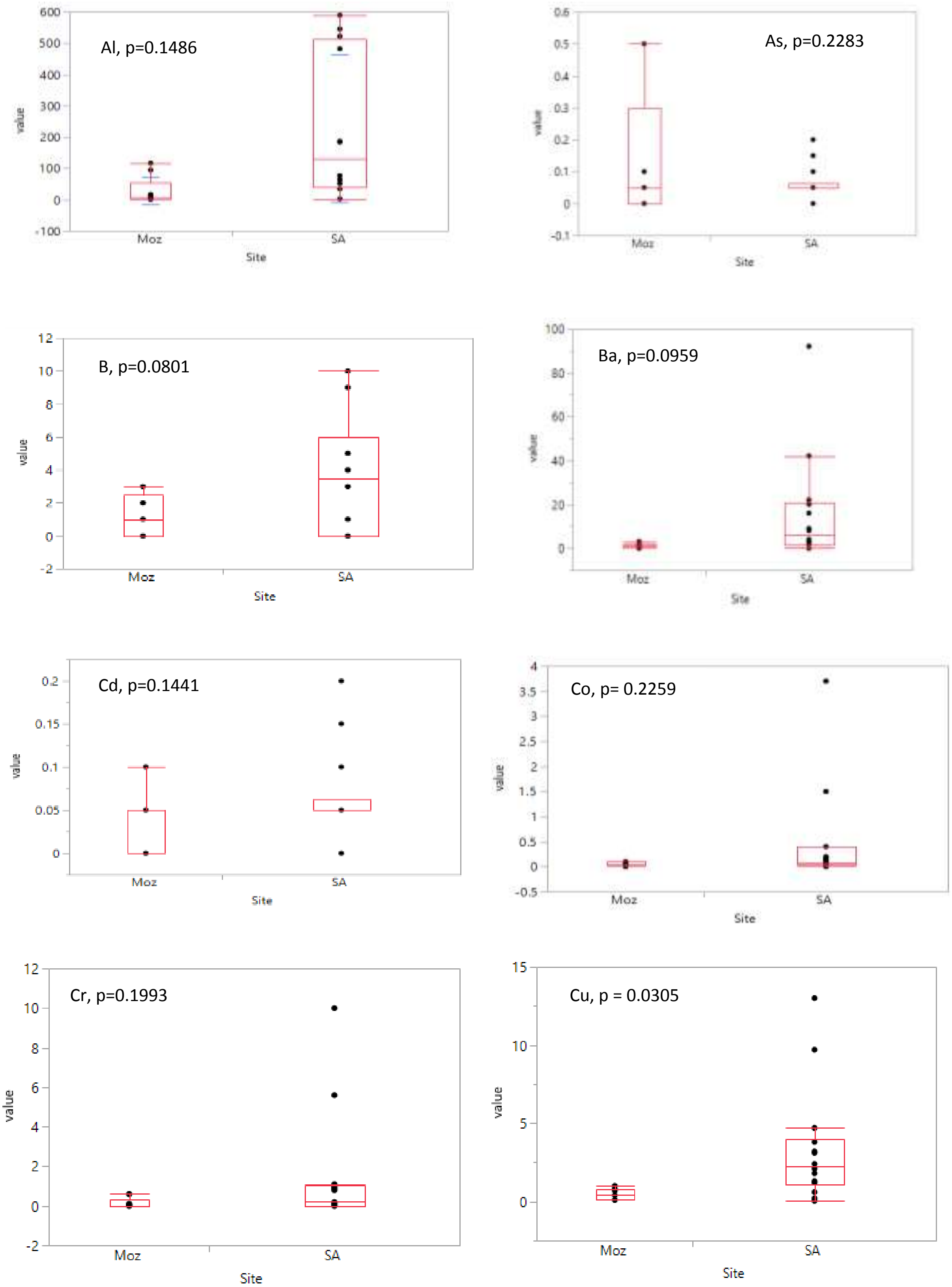


Figure S2a: ANOVA results of metals/metalloids in water samples in South Africa and Mozambique. Note: value = metal concentrations (µg/L). Top whisker: greatest value excluding outliers; Upper quartile: 25% of the data greater than this value; Median: 50% of data is greater than this value; Lower quartile: 25% of the data are less than this value; Bottom whisker: minimum value excluding outliers.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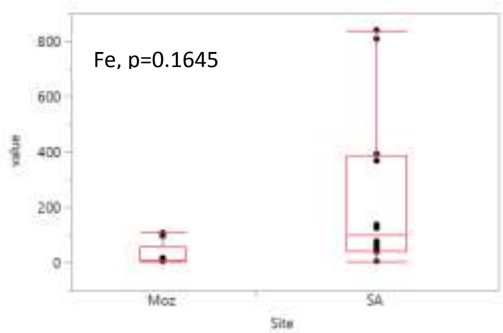
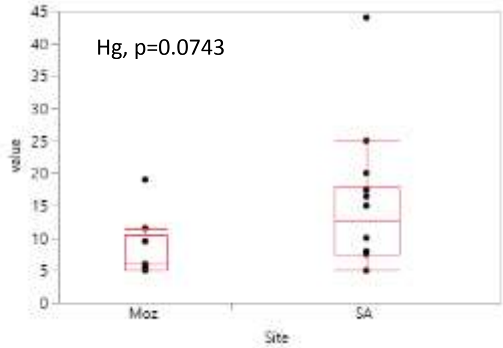
As, p=0.2283
B, p=0.0801
Ba, p=0.0959
Cd, p=0.1441
Co, p= 0.2259
Cr, p=0.1993
Cu, p = 0.0305
value
Site
Moz
SA


Fe, p=0.1645
value
Moz
SA
Site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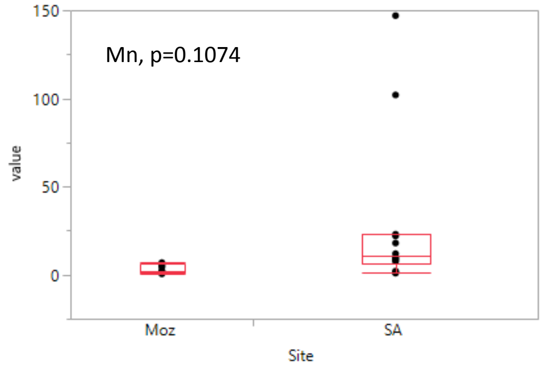
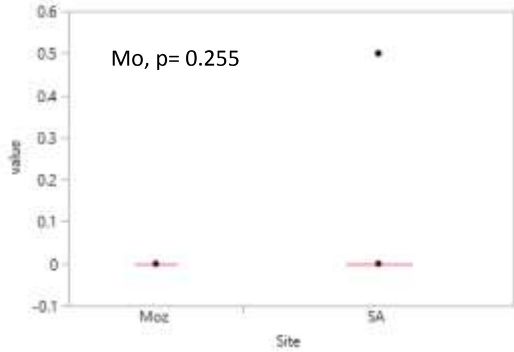
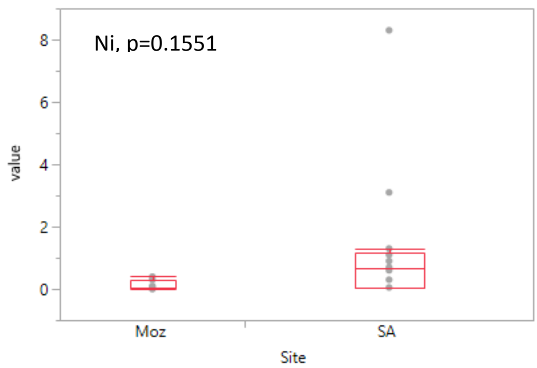
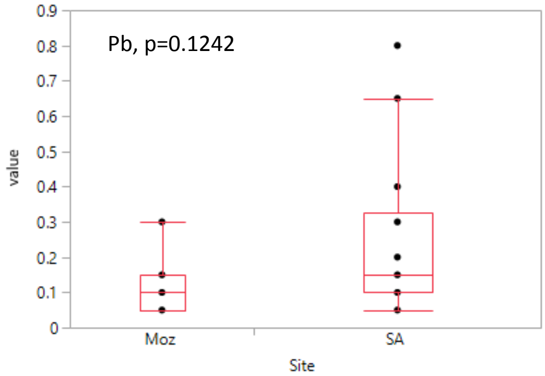
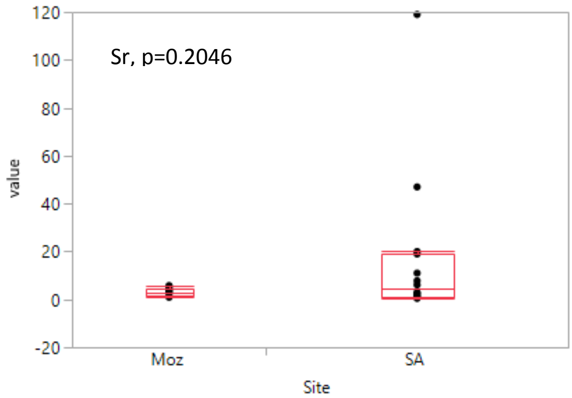
value
Moz
SA
Site


Mn, p=0.1074
value
Moz
SA
Site


Mo, p= 0.255
value
Moz
SA
Site


Ni, p=0.1551
value
Moz
SA
Site


Pb, p=0.1242
value
Moz
SA
Site


Sr, p=0.2046
value
Moz
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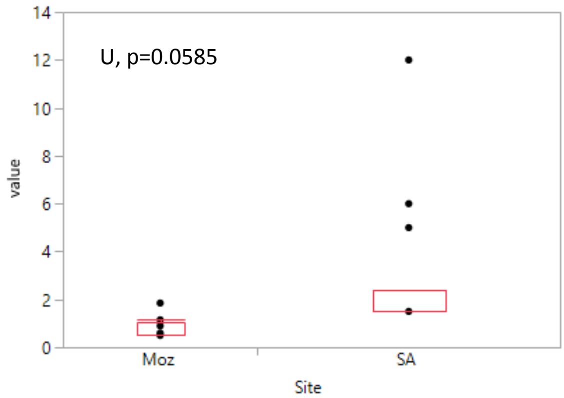
U, p=0.0585
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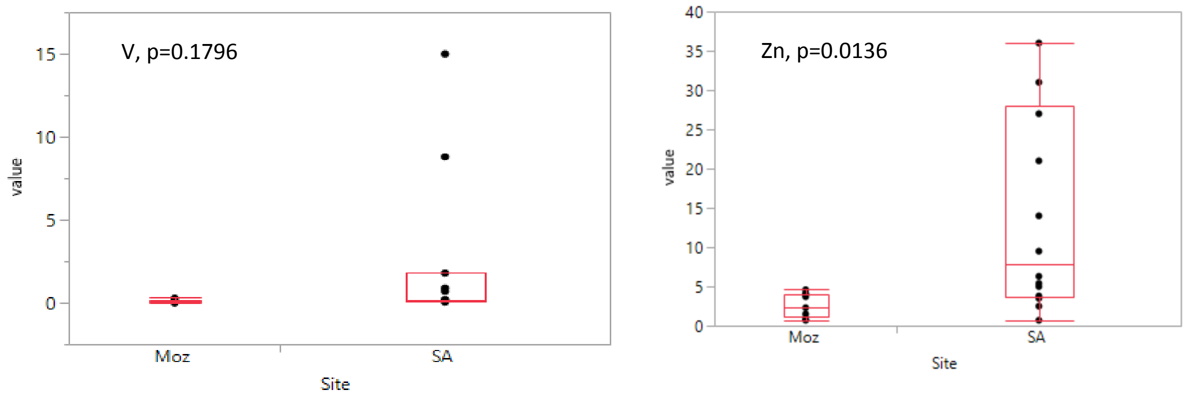

Figure S2b: ANOVA results of /metalloids vegetable samples in South Africa and Mozambique. Note: value = metal concentrations (mg/kg). Top whisker: greatest value excluding outliers; Upper quartile: 25% of the data greater than this value; Median: 50% of data is greater than this value; Lower quartile: 25% of the data are less than this value; Bottom whisker: minimum value excluding outliers.