

# Assessment of the Distribution and their Health Risk of Trace Metals in Tsaeda Agam River, Mekelle City, Tigray, Northern Ethiopia

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## Abstract

The study was conducted to assess the contamination of Tsada Agam River by trace metals. Trace metals were found in water samples in the following concentrations (in mg/L): Co, 0.02-0.03; Pb, 0.01-0.06; Zn, 0.21-0.50; Fe, 0.30-5.18; Mn, 0.10-0.15; Cu, 0.015-0.018 and Cd, 0.01-0.015. Trace metals were also found in soil samples (in mg/kg): Cu, 34.50-36.83; Pb, 1.17-3.42; Co, 29.75-31.53; Ni, 12.42-26.30; Mn, 616.06-811.30; Cr, 37.01-42.92; Cd, 13.87-14.55; Fe, 33563.53-3696 and Zn, 283.50-495.33. In vegetable samples the levels of trace metals were (in mg/kg): Cu, 3.00-14.67; Co, 9.33-38.31; Ni, 0.29-1.78; Mn, 30.93-346.90; Zn, 15.67-285.67; Pb, 0.14-2.67; Cd, 3.79-11.01; Fe, 46.67-730.00 and Cr, 2.53-5.72. Cadmium in water samples was beyond the limits of WHO/FAO for drinking and irrigation; Cd, Fe and Zn in soil samples was above the limits of Ewers and Zn, Pb, Cd, Fe and Cr concentrations in vegetables were above the limits given by Weigert. The calculated HRI values for Cd (Site-2 and 3) and Mn (site-1 and 3) were 1.4 and 1.7 and 2.0 and 3.78, respectively, indicating a health risk of Cd and Mn exposure. Therefore, regular monitoring of trace metals is essential to prevent excessive build-up in the food chain and to protect public health.

**Keywords:** Tsaeda Agam river; Soil; Vegetable; Trace metal; Health risk

## Introduction

In the last decades, human activities have resulted in a continuous increase in the levels of toxic trace metals in the environment. Anthropogenic activities such as agriculture, industry and urban life increase the concentration of these elements in soils and waters [1].

Trace metal contamination of streams and rivers is a worldwide environmental problem [2]. Trace amounts of metals may be present in fresh waters due to weathering of rocks and soils. Today, water quality monitoring has become a matter of great concern in stream and river water systems affected by disposal of urban effluents. Runoff, atmospheric deposition, domestic and industrial effluent discharges are the major sources of aquatic pollution [3].

In recent years the problem of urban soil contamination by trace metals emerged due to rapid industrialization and urbanization [4]. The modernization of industry and the presence of intensive human activities in urban areas have worsened the problem of trace metal contamination in urban soils [5]. The high concentrations of trace metals in urban soils have posed adverse effects on human health because metals can be easily transferred into human bodies from suspended dust or by direct contact [6]. Thus, trace metal contamination of the urban environment can have long-term and far-reaching environmental and health implications. Soil serves as both a sink and a source for trace metal contaminants in the terrestrial environment [7].

Excessive accumulation of trace metals in urban soils may result in increased human exposure to trace metals due to their close proximity to human activities. The investigation of the distribution of metals in soils and particularly in top layers allows effectively monitoring and assessing the pollution of soil itself and the overall environmental quality of soils [8]. Therefore, numerous studies of trace metal contamination in urban soils have been carried out. Soil pollution by trace metals is critical because they are not degradable, whereas organic pollutants or radionuclides have at least some degradation capacity. Metals occur in a number of different soluble and particulate forms, which influence their mobility and bioavailability. High contents of trace metals in soils

logically increase the potential uptake of these metals by plants. These metals are usually not essential for plant growth and after accumulating in the soil, they are transferred to food chain [9]. However, some metals like iron, manganese, cobalt, copper and nickel are essential nutrients; nevertheless, when they accumulate above their permissible limits they are also toxic for biological systems [10].

Leafy vegetables have the tendency to accumulate trace metals [11], partly because trace metals are non-degradable and persistent environmental contaminants, which may be deposited on the surfaces and then absorbed into the tissues of vegetables. Trace metal contamination of vegetables may also occur due to irrigation with contaminated water [12]. Emissions of trace metals from industrial sources and vehicles may be deposited on the vegetable surfaces during their production, transport and marketing. Prolonged consumption of unsafe concentrations of trace metals through foodstuffs may lead to a chronic accumulation of trace metals in the human kidney and liver, causing disruption of numerous biochemical processes such as cardiovascular, nervous, kidney and bone diseases [13]. In many regions including northern Ethiopia only limited data are available on trace metal concentrations in the vegetables [11,14,15]. Metals such as lead, cadmium and copper are cumulative poisons. These metals cause environmental hazards and are reported to be exceptionally toxic [16]. Several investigations of water, soil and vegetables in urban areas have demonstrated that these heavy metals are the main pollutants, particularly for soil irrigated with wastewater [12,17-22]. Thus, a

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detailed risk assessment of trace metal accumulation in agricultural lands is required. Therefore, this study aims to assess concentrations and risks of trace metals, and the environmental impact of the river water on the environment and in public health.

## Materials and Methods

### Description of study area

The study was carried out in Tsaeda Agam River, in and around Mekelle, Tigray, Northern Ethiopia. The city is one of the fastest growing urban areas in Ethiopia. The climate of the region is generally sub-tropical with an extended dry period of nine to ten months and a maximum effective rainy season of 50-60 days. Considering the rainfall, atmospheric temperature and evapo-transpiration, more than 90% of the region is categorized as semi-arid. This makes artificial irrigation using wastewater an attractive option for the region. The four sampling points of the study area were randomly selected using GPS (global positioning systems) (Figure 1): Site 1, approximately the sources of the river; Site 2, a market place near to the river; Site 3, a place where the river receives a liquid waste from Ayder Referral Hospital and Site 4, place where the river leaves the city.

### Instrument and chemicals

A drying oven with forced air and timer (FED 53, USA) was used for drying samples and A11 Basic Analytical MILL (IKA-Werke GmbH and Co.KG, 79219 Staufen, Germany) for grinding vegetables. A Varian AA240 FS Fast Sequential Atomic Absorption Spectrophotometer (FAAS) (Varian, Australia), fully automated and PC-controlled using

Apectra AA Base and PRO software versions and equipped with fast sequential operation for multi-element flame determinations, using four lamp positions and automatic lamp selection, was used for the determination of Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn.

The chemicals used were 70% HNO<sub>3</sub> (BDH, England), 70% HClO<sub>4</sub> (Aldrich, Germany), 37% HCl (Riedel-de Haen, Germany), and calibration standards SPECTROSCAN, Industrial Analytical (pyt) Ltd, South Africa) for the metals Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn.

The accuracy of analytical procedures was checked by analyzing certified reference material (IPE682 for plants; GBM908-2) and G310-10 for soils wheat (straw)/Triticum aestivum (Wageningen Evaluating Programs for Analytical Laboratories, The Netherlands) obtained from Ezana Mining Development P.L.C. Analytical Laboratory (Mekelle, Ethiopia). All samples and standards were diluted with deionized water.

### Collection, preparation and digestion

Samples of water, vegetables and soil were collected twice from the selected locations in February and March 2013, prepared and preserved in the laboratory until analysis was done.

**Water samples:** River water samples were collected in 250 mL plastic bottles from Tsada Agam River. Samples from the four selected locations were brought to the laboratory, centrifuged to remove the suspended particles, filtered through 0.45 mm micropore filter sand and preserved with 1.0 mL 70% HNO<sub>3</sub>. The filtered samples were stored in a refrigerator to minimize volatilization and biodegradation between sampling and analysis [23].

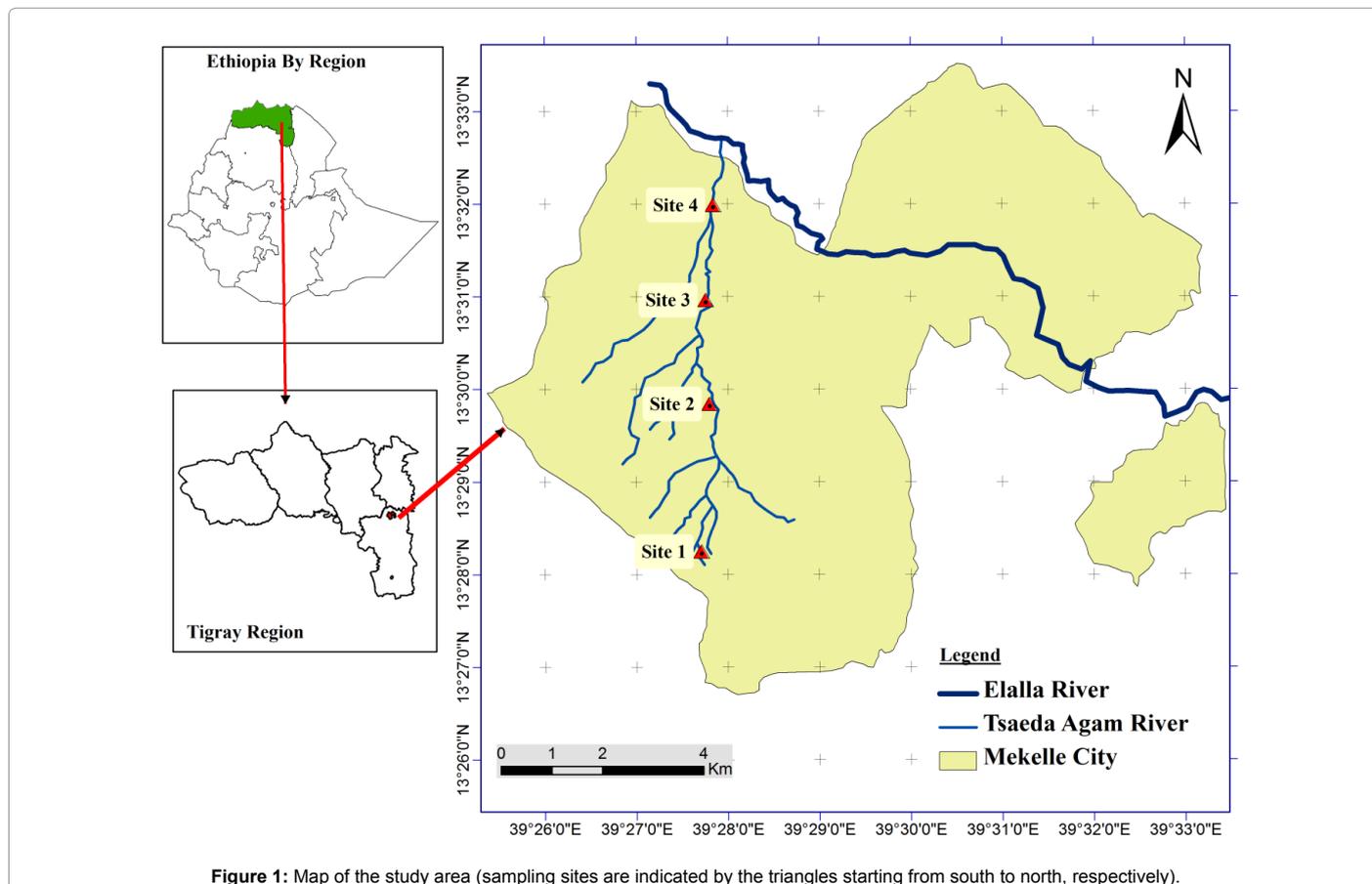


Figure 1: Map of the study area (sampling sites are indicated by the triangles starting from south to north, respectively).

Triplicate 50 mL water samples with a reagent blank were collected in a 250 ml conical flask; 10 mL nitric acid was added to each. The samples were then heated for two hours at 80°C. The mixture was allowed to settle for 15 h. The supernatant was analyzed for total Fe, Cd, Cr, Pb, Co, Ni, Cu, Mn, and Zn using FAAS [18].

**Vegetable sample:** Composite samples of vegetable Spinach (*Amaranthus caudatus*), which is mostly grown and consumed by the community living along the river, were collected from the study agricultural plots depending on availability. The samples were brought to the laboratory in paper bags, cleaned with deionized water to remove dust and extraneous matter and dried in an oven at 105°C for 12 h. The dried vegetable samples were ground and sieved through a sieve with 1 mm mesh size [18]. The dried sample was then homogenized and stored in tightly closed clean sample bottles until analysis.

Triplicate 0.5 g of dried powdered vegetable samples were mixed with 2.0 mL 30% H<sub>2</sub>O<sub>2</sub> into a test tube and digested at 150°C on a hot plate for 30 min. Then 2.0 mL HNO<sub>3</sub> was added to the sample and further digested on the hot plate for another 30 min. Digestion was continued with 2.0 mL of HClO<sub>4</sub> for 30 min, cooled, carefully transferred into a 50 mL volumetric flask, rinsed and diluted with distilled water and shaken. Finally, a sample was taken by 16 × 150 mm test tubes and analyzed for trace metals using FAAS [11].

**Soil samples:** Composite soil samples were collected randomly, from four agricultural plots with a stainless steel auger at 0-15 cm depths and stored in plastic bags. About 1 kg of each composite soil sample was taken from four study sites and thoroughly mixed; subsamples were taken at random sampling sites within the study area. All samples were well mixed, riffled and one-fourth of each sample was dried in an oven at 105°C for 12 h. The dried soil samples were ground and sieved through a sieve with 1 mm mesh size and analyzed.

Triplicate samples of 0.5 g of dried and powdered soil were transferred to a 50 mL conical flask and 5 mL concentrated sulfuric acid was added to each flask, followed by 25 mL concentrated nitric acid and 5 mL hydrochloric acid. The conical were heated at 200°C for 1 h. The sample was removed from the hot plate before becoming dry, cooled and diluted with 20 mL distilled water. The mixture was shaken and poured back to the beaker and settled for 30 min. Finally, a supernatant sample was taken by 16 × 150 mm test tubes and analyzed for trace metals using FAAS.

### Analytical procedures

Stock standard solutions containing 1000 mg/L of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (SPECTROSCAN, Industrial Analytical (pty) Ltd, South Africa) were used for preparing working standards (0, 0.25, 0.50 and 1.0 mg/L). Using a micro pipette, exactly 1.00 mL of the 1000 mg/L stock standard was poured into a labeled 100 mL volumetric flask; 20 mL concentrated hydrochloric acid (Analytical Reagent) was added to the flask and diluted to the mark with distilled water. Then 0, 2.5, 5.0 and 10.0 ml of 10 mg/L working standard was added in clean 100 mL volumetric flasks for preparing 0, 0.25, 0.50 and 1.00 mg/L standards, respectively. Analyses of the vegetables, soil and water samples were performed after determining the detection limits and validating the procedures with recovery tests.

### Method detection limits

The detection limits for analytical methods for water, soil and vegetable were obtained from three times the pooled standard

deviation, i.e., ± 3 s of six determinations of the reagent blanks as per Fifield and Kealey [24]. Instrument working conditions and detection limits are presented in Table 1.

**Validation of the analytical data using recovery test:** A recovery study was carried out by using standard reference material obtained from Ezana mining development PLC, Mekelle, Tigray, Ethiopia. The mean of each of the elements analyzed for the certified reference material (IPE682 for plants; GBM908-2 and G310-10 for soils) is given in Table 2; the recovery values were within acceptable ranges. The means are compared with the corresponding certified values using a student t-test at 95% confidence interval to determine the acceptability of the test results. The critical t test value for n=9 at 95% CI is  $t_{0.95}=1.859$  and for n=6 at 95 percent the confidence interval is  $t_{0.95}=2.015$ . The actual value of t was calculated using:

$$t_{calc} = \frac{|\mu_x - \mu_{crm}|}{\sqrt{\frac{s_x^2}{n} + \sigma_{crm}^2}}$$

Where n refers to the number of determinations,  $\mu_x$  is the analysis mean,  $\mu_{crm}$  is the certified mean,  $s_x$  is the standard deviation, and  $\sigma_{crm}$  is the certified standard deviation.

### Health risk assessment

The transfer factor, TF, was calculated based on the total metal content of the leafy part of the plant by using the formula stated by Khan et al. [20]:

$$TF = \frac{\text{Concentration of metal in edible part}}{\text{Concentration of metal in soil}}$$

The daily intake of metals was calculated to estimate the daily metal loading into the body system of a consumer (with specified body weight) [20]. This defines the relative phyto-availability of metal and does not take a possible metabolic removal of the metals into account, but indicates the possible ingestion rate of a particular metal.

There are many methods for estimating the daily intake of vegetables by the consumer based on health risk assessment; a common method is the Provisional Tolerable Daily Intake (PTDI). The PTDI is a reference value established by WHO [25] in which the vegetable diet per person and per day is 116.7 g. The daily intake of metal in this study was calculated based on the formula proposed by Khan et al. [20]. The daily intake was calculated as:

$$\text{Daily intake of Metal (DIM)} = \frac{Cm \times CF \times DIV}{BW (\text{average body weight})}$$

Where Cm is the concentration of a heavy metal in plant material (mg/kg), CF is the Conversion Factor (0.085), DIV is the approximate Daily Intake of Vegetables and BW is the average body weight (65 kg) [20].

The health risk index (HRI) was determined as the ratio of DIM and a reference oral dose ( $R_fD$ ) [13]:

$$HRI = \frac{DIM}{R_fD}$$

### Statistical analysis

All data were statistically analyzed by evaluating the mean and standard deviation. Water, vegetable and soil quality standards and the related legislation were used as a reference. The variation of each parameter between sites was analyzed using one way ANOVAs at P < 0.05 level of significance. All statistical tests were performed using SPSS software (SPSS Ins., version 20).

Element	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Lamp current (mA)	4	7	7	4	5	5	4	5	5
Fuel	C <sub>2</sub> H <sub>2</sub>								
Support	air								
Wave length (nm)	228.8	240.7	357.9	324.7	248.3	275.9	232.0	217.0	213.9
Slit width (nm)	0.5	0.2	0.2	0.5	0.2	0.2	0.2	1.0	1.0
Instrument detection limit	0.002	0.005	0.006	0.003	0.006	0.002	0.010	0.010	0.001
Water (mg/l)	0.01	0.01	0.02	0.01	0.02	0.02	0.03	0.01	0.5
Soil (mg/kg)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Vegetable (mg/kg)	0.01	0.01	0.02	0.01	0.02	0.02	0.03	0.02	0.05

Table 1: Instrument working condition and detection limits.

Metals	Plant CRM IPE682						Soil Certified reference material						
	Reference value, mg/kg		Measured Value, mg/kg, n=9		% Recovery	t-test	CRM	Reference value, mg/kg		Measured Value, mg/kg, n=6		% Recovery	t-test
	Mean	Std dev	Mean	Std dev				Value	Std dev	Mean	Std dev		
	Cu	2.2	0.706	2.15	0.22	97.7	0.070	GBM908-2	56	5	53.7	5.42	95.9
Zn	10.5	2.06	10.43	1.72	99.3	0.033	GBM908-2	70	24	63.44	15.16	90.6	0.265
Pb	6.77	0.874	7.12	0.89	105.2	0.379	GBM908-2	18	7	16.2	7.54	90.0	0.235
Ni	0.32	0.123	0.36	0.04	112.5	0.323	GBM908-2	26	8	23.7	1.49	91.2	0.287
Co	0.06	0.013	0.07	0.01	116.7	0.745	GBM908-2	21	7	19.6	1.43	93.3	0.199
Mn	21.5	2.27	24.77	3.29	115.2	1.297	Spiking	700	nr	721.4	9.96	103.1	nc
Fe	114	17	132.6	17.5	116.3	1.035	G310-10	4.88	nr	4.75	0.64	97.3	nc
Cr	0.62	0.153	0.59	0.06	95.2	0.194	G310-10	96	nr	87.5	15.4	91.1	nc
Cd	0.32	0.028	0.33	0.04	103.1	0.322	G310-10	5	nr	4.76	1.47	95.2	nc

Table 2: Validation of the analytical method using plant and soil certified reference materials (mg/kg dry wt.), nr refers to CRM standard deviation not reported and nc refers to t-test not calculated.

## Results and Discussion

### Trace metals concentration in water, soil and vegetable samples

The mean concentrations of trace metals in water, soil, and vegetable samples are presented in Tables 3, 4 and 5 respectively.

The mean concentration of Cd in the river water ranged from  $0.01 \pm 0.00$  to  $0.015 \pm 0.005$  mg/L while it varied in soil and in spinach (in mg/kg) between  $13.87 \pm 4.10$  to  $14.55 \pm 4.73$  and  $3.79 \pm 0.110$  to  $11.01 \pm 0.06$ , respectively. The range obtained for water is above the WHO and FAO recommended permissible limit of drinking water and irrigation water [25,26]. The level of Cd obtained in the soil samples were also above the maximum recommended limit set by Ewers [27] for agriculture soil and in the vegetable sample above the permissible limit set by FAO/WHO [13]. This is due to improper disposal of municipal as well as domestic waste and sewage from garages and construction works. The cadmium concentration in water and soil shows no significant variation (at  $p < 0.05$ ) but for spinach it varies between sites. This might be due to several factors which regulate the movement of cadmium from the soil to the edible part of the vegetable, i.e., soil pH, cation exchange capacity, soil organic content, soil texture, and the interaction of soil plant root-microbe.

The concentration of Co in the river water ranged from  $0.02 \pm 0.008$  to  $0.03 \pm 0.015$  mg/L while in soil and vegetable (in mg/kg), it varied from  $29.75 \pm 20.20$  to  $31.33 \pm 20.31$  and  $9.33 \pm 0.57$  to  $38.31 \pm 1.63$ , respectively. These values are below the WHO and FAO recommended limit set for drinking and irrigation water [25,26]. The concentration in spinach and in soil was below the recommended limit for the concentration of trace metals in vegetables and soils given by Weigert and Ewers [27,28]. The trace metal concentrations in soil and water were not significantly varied at  $p < 0.05$  between sites but varied

significantly between vegetables. This could be due to the physico-chemical nature of the vegetable growing soil. One of the major factors governing metal availability to plants in soils is the solubility of the metal associated with the solid phase. In order for root uptake to occur, a soluble species must occur adjacent to the root membrane for some finite period. The rate of release and the form of this soluble species will have a strong influence on the rate and extent of the metal uptake and may affect the mobility and toxicity in the plant.

Lead is highly toxic and harmful even in small quantities causing brain damage, particularly to the young and induces aggressive behavior [29]. Exposure to lead caused through air respiration (inhalation), water contamination from lead piping and from polluted fish. Lead toxicity occurs because it mimics many aspects of the metabolic behavior of calcium and inhibits many enzyme systems. The lead level in water samples varied between  $0.01$  to  $0.06 \pm 0.05$  mg/L, while in soil and vegetables (in mg/kg), it varied from  $1.50 \pm 0.49$  to  $3.42 \pm 1.42$  and  $0.14 \pm 0.04$  to  $2.67 \pm 0.65$ , respectively. The level of Pb obtained in the water from site-3 and site-4 were higher than the WHO recommended limit of drinking water but below the limit set for irrigation water by FAO [26] and irrigation soil by Ewers [28]. The concentration of lead was also below the maximum permissible limit of heavy metals concentration in vegetables described by FAO/WHO [13]. In site-3 the concentration of lead was higher than the concentration in soil which might be because Pb in the leaves of vegetable resulted from more diffuse anthropogenic sources. The results show that the concentration of lead in water and soil were not significantly different in between sites but the lead concentration in vegetable samples differs significantly (at  $p < 0.05$ ) suggesting a local variation in waste disposal along the river.

The concentration of Zn in water ranges between  $0.21 \pm 0.09$  and  $0.49 \pm 0.006$  mg/L, which is below the recommended limit given by WHO and FAO for drinking water and irrigation water [25,27]. The concentration of zinc in soil and vegetables (in mg/kg) varied from

Site	Cu	Zn	Pb	Cd	Co	Ni	Mn	Fe	Cr
Site1	0.015±0.005	0.21±0.09	0.01±0	0.01±0	0.02±0.008	BLD	0.15±0.06	1.36±1.18	BLD
Site 2	0.015±0.005	0.33±0.07	0.01±0	0.02±0.005	0.03±0.02	BLD	0.15±0.006	1.10±0.82	BLD
Site3	0.016±0.005	0.5±0.006	0.05±0.006	0.01±0	0.02±0.01	BLD	0.10±0.04	0.30±0.04	BLD
Site4	0.018±0.004	0.33±0.22	0.06±0.05	0.01±0.004	0.03±0.02	BLD	0.13±0.04	5.18±3.20	BLD
Guideline value for drinking water (WHO) <sup>a</sup>	2.0	3.0	0.01	0.003	-	0.07	0.40	-	0.05
Guideline value for irrigation water (FAO) <sup>b</sup>	0.20	2.0	5.0	0.01	0.05	0.20	0.20	5.0	0.10

<sup>a</sup>Source: WHO, 2008; <sup>b</sup>Source: FAO, 2011; BLD is below detection limit of the method [13,25]

**Table 3:** Trace metal concentrations (Mean ± SD) in water samples (in mg/L).

SITE	Cu	Zn	Pb	Cd	Co	Ni	Mn	Fe	Cr
Site 1	34.50±3.15	318.17±184.85	2.49±1.52	13.94±3.85	29.75±20.20	12.42±3.38	633.49±39.81	33563.56±3206.68	37.01±25.20
Site 2	36.83±3.71	495.33±241.77	3.424±1.42	14.55±4.73	30.56±18.50	20.61±5.79	616.06±48.53	36966±2384.45	39.432±24.34
Site 3	34.67±1.03	320.50±61.79	1.17±0.19	14.50±3.58	31.39±20.14	25.58±5.62	683.94±40.66	35464.67±1287.91	42.92±18.14
Site 4	36.50±3.21	283.50±107.13	1.50±0.49	13.87±4.10	31.53±20.3	26.30±2.28	811.3±175.25	36231±566.36	40.14±20.71
Guideline values <sup>c</sup>	100	300	100	3.00	50.0	50.0	2000	5000	100

<sup>c</sup>Source: Ewers [27]

**Table 4:** Trace metal concentrations (Mean ± SD) in soil sample (in mg/kg).

Site	Cu	Zn	Pb	Cd	Co	Ni	Mn	Fe	Cr
Site-1	14.67±3.05	105.67±17.21	0.14±0.04	10.28±0.67	38.31±1.63	0.29±0	184.71±1.99	416.67±35.12	2.68±0.21
Site-2	12.33±1.53	122.30±22.37	1.16±0.15	9.40±0.62	34.71±0.92	0.85±0.40	85.08±8.84	730±80.91	2.53±0.26
Site-3	11.00±1.00	285.67±31.53	2.67±0.65	11.01±0.06	37.33±0.85	1.78±0.52	346.90±4.28	585.67±662.08	2.67±0.26
Site-4	3.00±0	15.67±1.15	1.22±0.23	3.79±0.11	9.33±0.57	0.23±0.06	30.93±0.64	443.10±2.46	5.72±0.07
Guideline value	70.0 <sup>d</sup>	100	0.30 <sup>e</sup>	0.20 <sup>f</sup>	50.0	70.0	500 <sup>e</sup>	425	2.30

<sup>d</sup>Source: Weigert, 1991; <sup>e</sup>Source: Pendias and pendias, 1992; <sup>f</sup>Source: FAO/WHO, 2011 [13,28,32]

**Table 5:** Trace metal concentration (Mean ± SD) in spinach vegetable (in mg/kg).

283.50 ± 107.13 to 495.33 ± 241.77 and 15.67 ± 1.15 to 285.67 ± 31.53, respectively. Therefore, the findings indicate that in all studied sites except in site-4 the concentration of zinc in soil and spinach were above the maximum permissible limit for agricultural soil [27] and for vegetables, as described by Weigert [28]. The concentrations of zinc in vegetables show a significant variation (at p<0.05) from site to site which could result from more diffuse anthropogenic sources at different sites. The lowest concentration of zinc recorded in site-4 might be due to self purification of the water along the course of the river and the highest concentration of zinc recorded in site-3 was attributed to the high level of effluent of the wastewater treatment plant at Ayder referral hospital.

The concentration of Ni in the river water was below the detection limit of the instrument, but the toxicity of Ni at low concentrations may relate to the fact that Ni can cause allergic reactions and that certain Ni compounds may be carcinogenic. The level of Ni in the soil and in vegetable samples (in mg/kg) varied from 12.42 ± 3.38 to 26.30 ± 2.28 and 0.23 ± 0.06 to 1.78 ± 0.52, respectively. The results were below the recommended limits for soil and vegetable given by Ewers [27] and Weigert [28], respectively. Although Ni is considered an essential element for plants and some animals, present in the enzyme urease, its role for humans is yet to be demonstrated. In contrast, Ni related health effects including renal, cardiovascular, reproductive and immunological effects have been reported.

The chromium concentration in the river water was recorded below the detection limit of the instrument. Though chromium is an essential trace nutrient and a vital component for glucose factor, Cr toxicity (especially in its hexavalent form) damages the liver, lungs and causes organ internal bleeding. The metal concentration in soil and spinach

samples (in mg/kg) varied from 37.01 ± 25.20 to 42.92 ± 18.14 and 2.53 ± 0.26 to 5.72 ± 0.07, respectively. Therefore, the findings indicate that the results are in good agreement with the recommended limits given by Ewers for soils and by Weigert for vegetables [27,28]. There was no significant variation among the sampling sites.

Iron has an essential role as a constituent of enzymes such as cytochromes and catalase, and of oxygen transporting proteins such as hemoglobin and myoglobin [30]. In fresh waters, iron is also an important nutrient for algae and other organisms. Due to its high abundance within the earth crust, iron is ubiquitous in all fresh water environments and often reaches significantly higher concentrations in water and sediments than trace metals. High iron concentrations in fresh waters have long been considered a problem. In domestic use, iron-enriched waters may induce rust formation on plumbing fixtures, the staining of laundry and a metallic taste in drinking water. Hence, much effort has been put into the retention of iron in drinking water. The mining of iron rich ores has caused the degradation of many river ecosystems. Excess of iron also influences the presence of bacteria (iron reducing) in fresh water [31]. It affects target organs like the liver, the cardio vascular system and the kidneys. In this study, Fe was found in water samples in the range of 0.302 ± 0.035 to 5.18 ± 3.203 mg/L. This was above the recommended WHO limit for drinking water and above the FAO limit for irrigation water. The concentration of Fe in soil and spinach (in mg/kg) was found to be in the range of 33563.56 ± 3206.68 to 36966 ± 2384.45 and 416.67 ± 35.12 to 730 ± 80.91, respectively. Therefore, the concentrations of Fe were above the recommended limits indicated by Ewers for irrigation soil and by Weigert for vegetables [27,28]. This high concentration could be due to geological effects or may have resulted from diffuse anthropogenic sources. The

Site		Cu	Zn	Pb	Cd	Co	Ni	Mn	Fe	Cr
Site-1	TF	0.42	0.33	0.06	0.73	1.28	0.02	0.29	0.01	0.07
	DIM	0.002	0.02	0.00002	0.002	0.006	0.00004	0.03	0.06	0.0004
	HRI	0.05	0.05	0.006	0.16	0.6	0.002	2	0.08	0.08
Site-2	TF	0.33	0.25	0.34	0.64	1.14	0.04	1.28	0.02	0.06
	DIM	0.002	0.02	0.0002	0.001	0.005	0.00001	0.01	0.11	0.0004
	HRI	0.05	0.06	0.06	1.4	0.5	0.0006	0.92	0.16	0.08
Site-3	TF	0.33	0.89	1.78	0.75	1.19	0.03	0.53	0.02	0.06
	DIM	0.002	0.04	0.0004	0.002	0.006	0.0003	0.05	0.09	0.0004
	HRI	0.04	0.14	0.11	1.7	0.6	0.02	3.78	0.13	0.08
Site-4	TF	0.08	0.06	0.8	0.97	0.29	0.009	0.04	0.01	0.14
	DIM	0.0005	0.002	0.0002	0.0006	0.001	0.00003	0.005	0.07	0.0008
	HRI	0.02	0.08	0.06	0.6	0.14	0.002	0.36	0.1	0.02

**Table 6:** Transfer Factor (TF), Daily Intake of Metals (mg) (DIM) and Health Risk Index (HRI) of trace metals via intake of spinach vegetable grown using Tsada Agam River.

findings also showed significant variations in iron concentrations of spinach among sites, which might due to some soil factors/properties that affect the metal movement from soil to vegetable.

Copper in the aquatic environment is related to automobile traffic. Copper has a tendency to form complexes with organic species present in water. In stagnant water, Cu ions interact with organic species (coming from industrial waste) having a potential complexation ability to precipitate on the river bed and further percolate towards the water table. A high concentration of Cu in water is toxic to the human body and causes hypertension, uraemia and also produces pathological changes in brain tissues. In this study, the concentration of Cu in water was in the range of  $0.015 \pm 0.005$  to  $0.018 \pm 0.004$  mg/L, which is below the recommended WHO limit for drinking water and the FAO limit for irrigation water [25,26]. The metal concentration in soil and spinach samples (in mg/kg) ranged from  $34.50 \pm 3.15$  to  $36.50 \pm 3.21$  and  $3.00 \pm 0$  to  $14.67 \pm 3.05$ , respectively. The finding was below the maximum limits given by Ewers for irrigation soils and by Weigert for vegetables [27,28]. There was a significant variation (at  $p < 0.05$ ) of copper in vegetables among sampling sites, which might be related to the nature of the soil.

Manganese is one of the most abundant metals in the Earth crust, usually occurring together with iron. It is used in the manufacture of iron and steel alloys, as an oxidant for cleaning, bleaching and disinfection (as potassium permanganate) and as an ingredient in various products. Manganese greensands are used in some locations for potable water treatment. Manganese is an essential element for humans and animals. In this study, the concentration of manganese in water was found in the range of  $0.10 \pm 0.04$  to  $0.15 \pm 0.06$  mg/L, which is below the recommended WHO limit for drinking water and the FAO limit for irrigation water [25,26]. The concentration of Mn in soil and spinach samples (in mg/kg) ranged from  $616.06 \pm 48.53$  to  $811.30 \pm 175.25$  and  $30.93 \pm 0.64$  to  $346.90 \pm 4.28$ , respectively. The obtained results were below the recommended limit of Ewers for irrigation soil and Pendas and Pendas for vegetables, respectively [27,32]. The high concentration of manganese in soil and vegetables could be due to geological effects or diffuse anthropogenic sources.

### Assessing health risk from consumption of vegetables

The transfer factor expresses the bioavailability of a metal at a particular position on a species of plant. This depends on different factors such as the soil pH and the nature of the plant itself. Different authors have reported different transfer factors for the same species of plant and across different parts of the plants, such as roots and leafy parts. A transfer quotient of 0.1 indicates that the plant is excluding the element from its tissues. The larger the transfer coefficient (larger than

0.5), the greater the chances of vegetables for metal contamination by anthropogenic sources [20]. Accordingly, only Fe (0.015), Ni (0.025) and Cr (0.083) are excluded in the plants tissue, which agrees with the high concentration of Fe in the soil, dropping significantly in the vegetable. Co has the highest transfer factor, with an average of 0.975; this might be attributed to the low retention rate of the metal in soil; Co is therefore more mobile in the soil (Table 6). The lowest TF was recorded for Fe with a transfer factor of 0.015 probably because it is a major component in the soil and therefore it binds more to the soil. In this study, the transfer pattern for metals is in the order of  $Co (0.975) > Cd (0.773) > Pb (0.745) > Mn (0.535) > Zn (0.383) > Cu (0.290) > Cr (0.083) > Ni (0.025) > Fe (0.015)$ . Variations in transfer factor among the studied trace metals may be attributed to differences in the concentration of metals in the soil and differences in element uptake by spinach [33,34].

In order to understand the health risk of trace metals, the food chain is the most important pathway to assess the exposure of humans to trace metals. The daily intake of metal for the studied spinach leafy vegetable is presented in Table 6. The consumption of spinach vegetable grown using Tsada Agam River has the highest DIM for Fe (0.083), Mn (0.024), and Zn (0.021) but this is nearly free of risks, as the dietary intake limits of Fe, Mn and Zn in adults can range from 10.0 to 50.0 mg, 2.0 to 20.0 mg and 5.0 to 22.0 mg, respectively [35]. The high DIM for these trace metals might be due to high concentrations of these metals obtained in spinach.

To assess the health risk associated with trace metal contamination of grown vegetables, the Health Risk Index (HRI) was calculated. The HRI for the studied trace metals such as Cu, Zn, Pb, Cd, Co, Ni, Mn, Fe, and Cr is presented in Table 6. If the value of HRI is below 1, the exposed population is assumed to be safe [20]. The results show that Cd and Mn contamination in spinach has the largest health risk to spinach consumers. The health risk index was more than 1 for Cd in site-2 and site-3 (1.4 and 1.7, respectively). For Mn, it was also higher than 1 in site-1 and site-3 (2.0 and 3.78, respectively). The value for Cd was high, possibly because Cd is considered as the most significant heavy metal affecting leafy vegetables. The population is therefore at greater risk of Cd and Mn exposure since their values are larger than 1. In the present study, Cu, Zn, Pb, Co, Ni, Fe and Cr were not found to cause any risk to the local population with the consumption of spinach vegetable grown using Tsada Agam River.

### Conclusion

Irrigation of urban agricultural lands with unsafe river water led to the accumulation of heavy metals in the soil and vegetables. This study

indicates variations in the trace metal level at different sampling sites due to the differences of geological or diffuse anthropogenic sources. Cd, Pb and Fe concentrations in the river water were found to be above the international permissible limits for drinking/irrigation purposes. Zn, Cd and Fe were also above the recommended limits of irrigation soil and Zn, Pb, Cd, Fe and Cr were above recommended limits for vegetables. The DIM and HRI of heavy metals also suggested that Cd and Mn contamination in spinach vegetable had potential for human health risk due to the consumption of the spinach vegetable grown with the Tsada Agam River water. Therefore, the consumption of vegetables with excess levels of trace metals may lead to high metal accumulation in the human body posing different health disorders. The study suggests that even though there are low trace metal concentrations in the river/irrigation water, its long term use can cause trace metal contamination through bioaccumulation in soils and vegetables resulting to health risk of vegetable consumers. Thus, urgent attention is needed for the full scale risk assessment on the use of unsafe water supply and water quality monitoring to regulate the urban waste disposal along the river banks for the sustainable use of Tsada Agam River. The study also suggests that great efforts and collaborations between different authorities are needed to protect the river from pollution and reduce environmental risk through a proper treatment of the agricultural, industrial, and sewage discharge.

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