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Potentially toxic elements status and distribution in Usangu agroecosystem-Tanzania

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ABSTRACT

This study was conducted to highlight status and distribution of potentially toxic elements (PTEs) in Usangu agroecosystem-Tanzania. The study involved 198 soil samples from 10 irrigation schemes including three land use. The concentrations of selected PTEs (Cd, Cr, Cu, Pb, Zn, As, Hg, Co, Nie etc.) were determined to estimate status, distribution, and contamination hierarchy. The total and bioavailable PTEs were determined by aqua regia digestion and Mehlich 3 methods, respectively. We observed variable total PTEs concentration (in mg/kg) among land use and irrigation schemes such as Cr (15), Co (2.9), Fe (7371), Mn (263), and Zn (18.2). Also, concentration of other PTEs (in µg/kg) were As (1382), Cd (22), Cu (3342), Hg (3.3), Ni (4107), and Pb (5661). It was observed that 99.5, 87, 66 and 12% of the studied soils had total Fe, As, Se and Hg concentration above allowable threshold in agricultural soils, respectively. The bioavailable PTEs fraction were lower than total values from different land use and irrigation schemes, higher values of bioavailable PTEs were associated with agricultural intensifications. The status of PTEs in Usangu agroecosystem observed to be at level potentially to cause damaging effect to soil invertebrates, plants, animals and human if remain unregulated. This study highlights baseline information and evidence for site-specific environmental management planning and a scientific basis required to establish PTEs management in agricultural soils to ensure health food and environmental safety.

1. Introduction

Potentially toxic elements (PTEs) includes elements which have toxicity effect on soil microbes, plants and animals especially when they are available in higher concentrations. Some PTEs are carcinogenic such as mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd), and arsenic (As) (Abdu et al., 2011; Addis and Abebaw, 2017). Some PTEs like iron (Fe), copper (Cu), manganese (Mn), zinc (Zn), cobalt (Co), and selenium (Se) at low doses are plant micronutrients. PTEs in agricultural soils are the potential route for PTEs to plants and food chain (Liu et al., 2007; Xu et al., 2017). Thus, PTEs accumulation in soil and plant materials can increase PTEs levels in human body via food (Chabukdhara and Nema, 2013; Phuong et al., 2010, 2008). High use of agro-echemicals in farming areas can elevate PTEs in soils and water because of high PTEs impurities associated (Lema et al., 2014; Lema and Mseli, 2017; Matowo et al., 2020; Philbert et al., 2019). The accumulation of PTEs in agricultural soils can contaminate crop grains leading to health risks to users. Countries like China reported that increased PTEs in agricultural soils because of increased use of agrochemicals and wastewater use with elevated PTEs (e.g. Cd, Pb, Hg, Cr). About 10 million tons of rice grain reported to be contaminated by PTEs per year in China (Teng et al., 2010). Increased use of agrochemicals increase the risk of PTEs accumulation in agricultural soils and water which later can spread to other ecosystem and food chain (Abdu et al., 2011; Abdullahi et al., 2014; da Silva et al., 2016; Goncalves et al., 2014; Lema et al., 2014).

The Usangu basin is important in agricultural sector and biodiversity in Tanzania including irrigation farming, national parks and game reserves (Fox, 2004; Kashaigili et al., 2006; Machibya and Mdemu, 2005). The location of Usangu basin (USB) allows fast offload of crop produces due to presence of Tanzania and Zambia highway (TAZAM) and Tanzania and Zambia Railway (TAZARA). But also, the basin is close to rapid growing city of Mbeya and receives runoff from urban areas and Kipengere mountain range which is used for irrigation (Katambara et al., 2016; Malley et al., 2017). Runoff water from urban cities, TAZAM and TAZARA lines are sought to have elevated levels of PTEs and nutrients. Studies by FBD (2007) and Fox (2004) on water quality from rivers in Usangu basin in December 1999 reported elevated levels of PTEs in runoffs (i.e., Cu 10 µg/L; Cd 10 µg/L; Cr 10 µg/L; Pb 10 µg/L; Zn 20 µg/L; Co 10 µg/L; and Ni 10 µg/L and plant nutrients such as K 8900 µg/L; Na 157,000 µg/L; Ca 9700 µg/L; Mg 4500 µg/L; Fe

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3200 μg/L; Mn 10 μg/L and pH of 6.8). Elevated levels of PTEs and plant nutrients in rivers were reported to be influenced by urbanization and agricultural intensification in the nearby areas, i.e., Uyole, Chimala, and Igurusi (Machibya and Mdemu, 2005). Usangu agroecosystem since 1985 have experienced incredible intensification by involving increased number of crops grown per season and agrochemicals uses (Cox, 1985; Machibya and Mdemu, 2005; Matowo et al., 2020; Philbert et al., 2019). This practice increase land productivity but also pose ecological and environmental challenge of contamination and pollution risks. The contaminated downstream from Usangu basin lead to environmental impacts such as siltation of some rivers draining from irrigated areas and eutrophication of wetlands donwstream of the irrigation areas affecting whole water budget of the Great Ruaha River downstream of N'Giriama but also the area is a hot spot for bilharzia disease (Elisa et al., 2021; Kihwele et al., 2018, 2021). Therefore, assessment of PTEs in water and agricultural soils in Usangu agro-ecosystem is vital for quality assessment and management since no up-to-date information on PTEs status and distribution in the area which limits PTEs strategic management in agroecosystem. This study was conducted characterize soil PTEs status and distribution in Usangu agro-ecosystem for monitoring and sustainable land management.

2. Material and methods

2.1. Study area

The study was conducted in the Usangu Basin (USB) Mbeya-Southern Highland Tanzania, located between latitudes 7°41´and 9°25´ South and longitudes 33°40´ and 35°40´ East with an area of 20,800 km^2. The area has average annual rainfall of 1000–1600 mm. In the north it has an area wide flat plain with alluvial soils supporting irrigated and dry land farming. The basin receives rainfall from December to March and seven dry month. The downstream from Usangu runs to Great Ruaha River, Ruaha National Park to Mtera and Kidatu dams (Fig. 1).

2.2. Description of the study area and farming management

The study were conducted in ten irrigation schemes (Moto mubaya, Igalako, Ihahi, Chimala, Uturo, Kapunga, Utengule-usangu, Mwatenga/Ilaji, Mubuyuni, Isenyela and Mabadaga). The schemes in the area were classified as (i) Group I:-purely agriculture (pure agriculture schemes) which have farms only and no settlements. This includes A-Utengule usangu, B-Kapunga, C-Mubuyuni, Uturo, Isenyela and Mabadaga and F-Mwatenga (Fig. 2). Group I schemes have well-established irrigation systems with concrete irrigation channels from major rivers; schemes are highly mechanized and intensified for high yields and increased inorganic fertilizer use (Carvalho, 2015; Ngailo et al., 2016; Nonga et al., 2011). (ii) Group II:-mixed agriculture schemes where includes farming areas and scattered rural settlements (such as D-Ihahi, and-Chimala, E-Igalako and Mahongole) (Fig. 2). The Group II schemes are situated in farming areas and scattered rural/town settlements in between, which positively or negatively influence PTEs concentration and distribution in agricultural soils. The area mainly involves smallholder farmers with less agrochemical utilization, organic manure and inorganic fertilizer application. The scheme category might influence the concentration and distribution of PTEs in topsoils in agricultural fields (Kibassa et al., 2013; Mwegoha and Kihampa, 2010; Shemdoe, 2010). The settlements around the area might influence soil quality due to waste disposals from domestic and urban effluents. The land tenure in this group is mainly local ownership which might influence soil quality due to management. In each group, reserved areas (conserved areas) were collected to save as reference points.

2.3. Soil sample collection, extraction and quality assurance

Soil samples were collected in Group I and II, where 198 soil samples were collected in 66 sampling points from November to December 2019 at 0–30 cm depth. Collected samples were air dried and ground to pass 2 mm sieve. All analyzes were conducted at University of Plymouth-United Kingdom where total and bioavailable PTEs were determined as follows;

Total PTEs concentration (AQ); Soil samples were digested in acid mixture of HCl and HNO_3 (aqua regia (AQ)) from Sigma-Aldrich Chemie GmbH in a ratio of 3:1 in a hot plate for at least three hours (UoP, 2015). Approximately 0.2 g of soil sample was weighed and placed in a 25 ml beaker. One (1) ml of high purity HNO_3 were added to the beaker and allowed to cold digest for 1 hour. After one hour, 3 ml of high purity HCl and additional 1 ml of HNO_3 were added and allowed to hot digest (95–100 °C) for at least 3 h until the brown fumes stopped evolving. Then sample allowed to cool and filtered into 25 ml volumetric flask using an acid-resistant filter (Whatman filter No.42) and made to the mark with 2% HNO_3 and stored at 4°C until analysis.

Bioavailable PTEs (M3); The bioavailable PTEs were extracted by Mehlich 3 extraction solution (M3) (Guo, 2009; Mehlich, 1984). Two grams of air-dried soils were weighed and placed in 50 ml centrifuge tubes, 20 ml of M3 solution were added and tied, shaken in a mechanical shaker at 180 rpm for five minutes. The mixture was centrifuged at 1200 rpm for 5 min and filtered into a 10 ml volumetric flask through an acid-resistant filter.

Quality Assurance (QA): To ensure reliability of data, reagent blanks, standard reference material (SCP- S150123029 and SS2 EnvironMAT-S150827031) were used to monitor the determination quality in Mehlich 3 and acid digestion method, respectively. Milli-Q water were used to prepare reagents and calibration standards. The 10% HNO_3 and 10% HCl, distilled and Milli-Q water were used to wash all glasswares to avoid contamination. All samples were extracted and measured in triplicate, the PTEs concentration in soil extracts were determined by ICP-OES and ICP-MS. The recovery of samples spiked with standards ranged from M3 (83% to 105%) and AQ (74.78% to 98.10%).

Soil contamination assessment: To assess PTEs soil contamination, regulatory values i.e., maximum allowable limit for PTEs in agricultural soils Tanzania (TZ) and USEPA values were used (Mclean and Bledsoe, 1992; URT, 2007). The obtained values were compared with regulatory values for PTEs contamination analysis. Any sample with a value exceeding the threshold limits were considered contaminated or highly to be contaminated (Table 2). The ratio of total PTEs concentration (AQ) with TZ and USEPA maximum limits (AQ:TZ, and AQ:USEPA) were computed to estimate contamination hierarchy. In addition the ratio of bioavailable PTEs (M3) and total PTEs (AQ) were computed (M3:AQ) to estimate PTEs bioavailability.

2.4. Statistical analysis

Statistical methods were applied to analyze the data in terms of its distribution and correlation among the studied parameters. All collected data were statistically analyzed by the Jamovi 1.2.25 and IBM SPSS Statistics 24 programs (IBM: Chicago, IL, USA). The computed mean values were compared to the regulatory values to evaluate the magnitude of contaminants in the environment. The statistical difference among irrigation schemes, land uses, and sampling points were determined by ANOVA, and Tukey posthoc tests ($P < 0.05$). Pearson correlation analyses were performed to analyze relationship of PTEs in soils. The study and sampling site were generated by QGIS 3.10.7 software.

3. Results and discussion

3.1. Total PTEs concentration

Total PTEs concentration among land use and irrigation schemes determined by acid digestion (AQ) varied significantly ($P < 0.05$) amongst

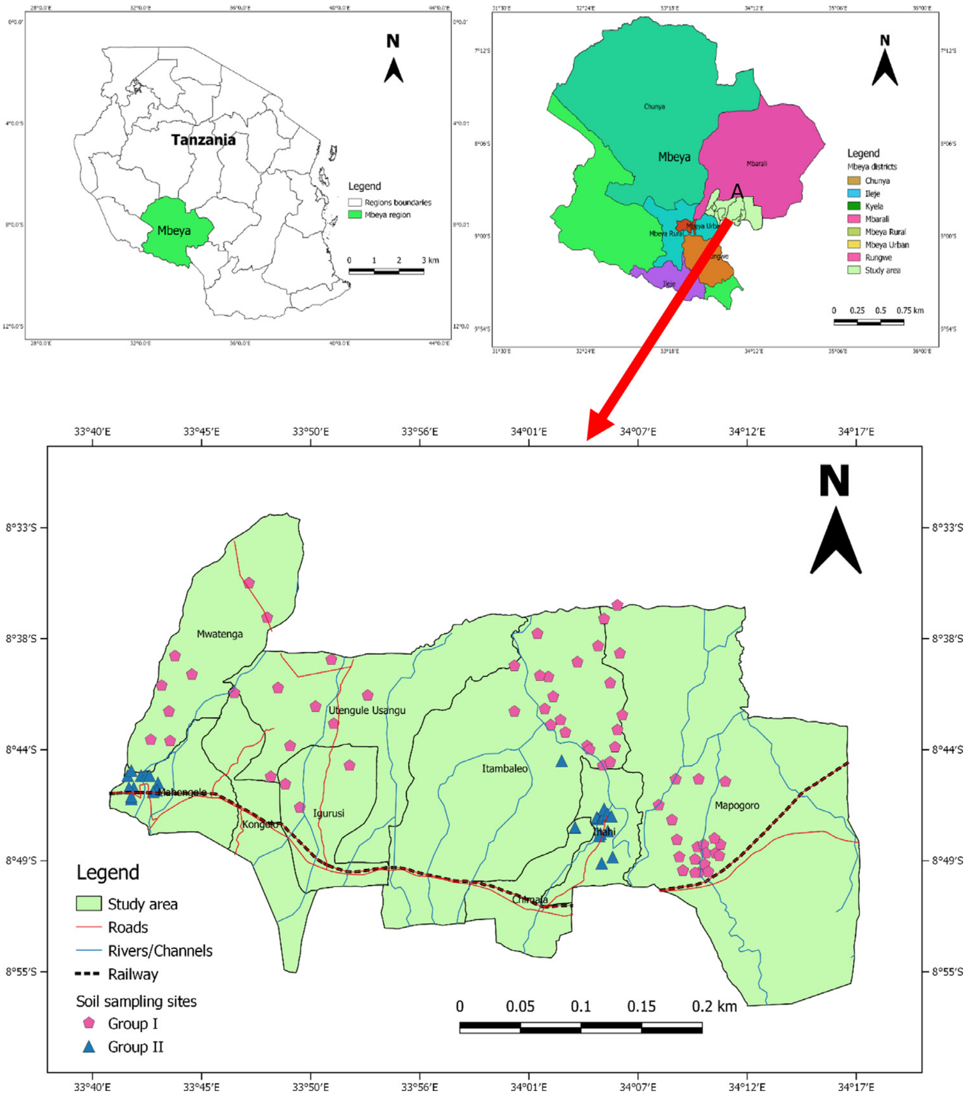

Fig. 1. Distribution of soil sampling sites in different irrigation schemes of the Usangu basin-Mbeya Tanzania.

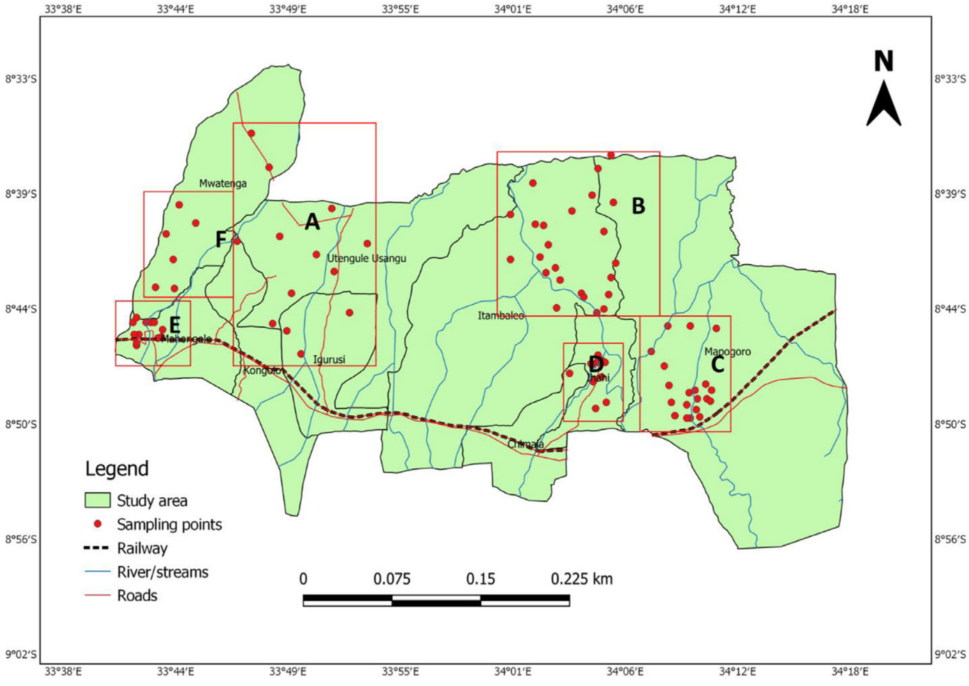

Fig. 2. Scheme classification in study area, where schemes A, B, C, and F are pure agriculture (Group I) and D and E are mixed agriculture schemes (Group II).

Table 1
Maximum allowable limit (mg/kg) of PTEs in natural habitat and agricultural soils in Tanzania (He et al., 2015; URT, 2007; USEPA, 2014).

S/N	PTEs	TZ (mg/kg)	USEPA (mg/kg)
1	As	1	0.2
2	Cd	1	0.1
3	Cr	100	1
4	Fe	50,000	–
5	Pb	200	0.1
6	Mn	1800	5
7	Hg	2	0.005
8	Ni	100	50
9	Se	20	20
10	Cu	200	2
11	Zn	150	5

sampling sites, land uses and irrigation schemes. The determined AQ-PTEs (mg/kg) were; Al (7887.03), Cr (15.39), Co (2.92), Fe (7371.18), Mn (263.14), and Zn (18.249). The other AQ-PTEs (in µg/kg) were Ag (36.54), As (1381.73), Cd (21.49), Cu (3342.39), Hg (3.28), Mo (281.88), Ni (4106.92), Pb (5661.04), Sb (27.34) and Se (2695.75). The determined PTEs values such as Co, Ag, Fe, Mo, As, Hg and Se in were above Tanzania maximum allowable limit of PTEs in agricultural soils (URT, 2007). PTEs such as Cr, Cd, Cr, Mn, Co, Zn, Mn, and Pb had values below the limit (Table 1). Among 198 collected soil samples, about 99.48%, 86.53%, 66.32% and 11.92%, of samples had Fe, As, Se, and Hg concentration above the threshold, respectively. This indicates that the system is somehow invaded by soil contamination which affect environmental quality and food safety. The comparison of determined PTEs values with USEPA maximum allowable limit most of the soils had AQ-PTEs concentration above USEPA maximum allowable limits. Therefore, management strategies have to be in place to avoid further PTEs increase in agricultural soils. The total AQ-PTEs determined for Pb, and Zn were lower than values reported elsewhere in the world. For example, the value for Pb (5.66 mg/kg) and Zn (18.249 mg/kg) was lower than values reported by Abdullahi et al. (2014) in soils in Birnin Gwari in Nigeria (Pb = 20.83 mg/kg and Zn = 61.82 mg/kg) and the AQ of Cu, Ni, Cd, Pb were observed to be lower than that reported by Shah et al. (2013) in Pakistan. However, the situation might change in the near future due to agricultural intensification and urbanization happening in the area.

Rationing the PTEs concentration in the study area with maximum TZ and USEPA allowable limits computed to estimate contamination or pollution hierarchy (Table 3) which observed to vary significantly ($P < 0.05$) among land uses and irrigation schemes. Comparing the concentration of PTEs determined with values determined by FBD (2007) and Fox (2004) in 1999 in the area, it was observed increase of PTEs in the area over time signifying the of anthropogenic activities in and nearby areas.

3.2. Land use and distribution of AQ-PTEs

The analysis of soil samples from maize farming, paddy farming, and conserved areas determined PTEs distribution in different land uses. It was observed that significantly higher PTEs concentrations ($P < 0.05$) were in farming areas than conserved areas (Table 2), which might be influenced by the farming practices and intensifications. The general trend of soil PTEs based on land use were higher in paddy farming (in Group II) ($P < 0.05$) than in maize farming areas. This is because of paddy farming intensification in the area involves ,high use of fertilizer and other agrochemicals (Ngailo et al., 2016). Generally, the conserved areas were observed to have a statistically significant lower PTEs concentration ($P < 0.05$) than the other two land use. Mean values (in mg/kg) of some PTEs were; Al in paddy (8018.24), maize (6540.72) and conserved area (7520.81); Cr in paddy (15.31), maize (13.34) and conserved area (17.89); Cd in paddy (21.06), maize (31.86), and conserved area (17.98); Pb in paddy farming (5.578 mg/kg), maize farming (6.324 mg/kg), and conserved area (6.039 mg/kg). When PTEs concentration in different land uses compared based on scheme classification (Group I and II), PTEs concentrations were statistically significantly different among groups, where in conserved areas Group II had higher PTEs, in maize growing areas Group I and in paddy farming Group II had higher PTEs concentrations (Table 2). Over the entire land use in the area, Group I had statistically higher values of Ag, As, Co, Cu, Ni and Cr while Group II had higher concentration of Se, Pb, Mo, Hg, and Cd (Table 3). The observed trend indicates that farming and related activities conducted in farming areas and in vicinity are largely responsible for increased PTEs in agricultural soils. This scenario supported by Moss (2008) and Tutic et al. (2015) who reported agricultural activities to contribute PTEs accumulation and pollution in an agro-ecosystem. The general trend of high PTEs concentration in farming areas than in conserved areas is an indication that agrochemicals, irrigation water and machines used or working in farming areas could be associated with increased PTEs.

Conserved areas recorded higher values in some parameters than those in maize farming areas (Table 2). For example, As in paddy farming (1261.23 and 1568.92 µg/kg for Group I and II), maize farming (1560.89 and 1404.61 µg/kg for Group I and II), and conserved area (1712.54 and 1671.79 µg/kg for Group I and II); and Cr in paddy farming recorded (16.43 and 12.58 mg/kg for Group I and II), maize farming (15.17 and 13.34 mg/kg for Group I and II), and conserved area (18.46 and 15.61 mg/kg for Group I and II) (Table 2), this indicates that higher PTEs values could be from wind deposition and runoffs from nearby towns which ends up in conserved areas. The same scenario was reported in Luanda Angola (Ferreira-Baptista and De Miguel, 2005) and Spain (Ordóñez et al., 2003; Ramos-Miras et al., 2011) where a high PTEs concentration were observed in reserved areas indicating that PTEs might be originated from different sources and transported as dust, aerosols and runoffs to the area. Natural sources are also a possible reason for higher PTEs in reserved areas; however, geological materials in the Usangu basin are not enriched with the elements detected (Delvaux and Hanon, 1993).

To estimate the contamination or pollution hierarchy, the ratio was computed between total PTEs and regulatory values (TZ and USEPA) (Tables 1 and 3). The computed pollution hierarchy ratio indicates that total concentration of Cr, Co, Fe, Mn, Zn, As, Ag, Mo, Cu and Pb were above USEPA maximum allowable limits (Table 3) which means the AQ:USEPA ratio was significantly greater than 1 ($p < 0.05$). Among 198 collected soil samples, 99.48%, 99.48%, 99.48%, 96.67%, 96.97% and 67.68%, and of Cr, Mn, Zn, As, Pb and Cu respectively were above USEPA maximum permissible limit for PTEs in agricultural soils. The AQ:TZ ratio as a pollution hierarchy computed observed that only concentration of Co, As, Ag, Mo and Fe (Table 3) were above the Tanzania maximum allowable limit for PTEs in agricultural soils and natural habitats. The higher PTEs concentration than the acceptable limits indicates that there is a risk of detrimental health effects to human and environment as some PTEs are carcinogenic (Defarge et al., 2018; Hu et al., 2021). Based on the pollution hierarchy, farming areas were more polluted or at risk compared to reserved areas. Therefore agricultural activities like fertilizer, pesticides, herbicides, and other agrochemicals application are likely to contribute to PTEs accumulation in agricultural soils. But also emission from machines and vehicles operating in farming areas, washing and bathing in irrigation canals is probable cause for an elevated PTEs levels in agricultural soils. Hence immediate action and monitoring program has to be in place to avoid a further increase in PTEs in agroecosystem. The significance difference in regulatory values among authorities prevent international cooperation in PTEs environmental conservation and managements of agro-ecosystems because an area can be classified contaminated by one country regulatory value but uncontaminated by other authority value thus delaying the immediate remediation actions.

Table 2
The AQ mean values for PTEs concentrations in soils in different land use in Usangu agro-ecosystem.

Land Use	Group	Al (mg/kg)	Cr (mg/kg)	Co (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Pb (µg/kg)
Conserved Area	I	6867.23	18.46	3.41	8183.00	269.40	19.12	5540.79
	II	10,135.16	15.61	4.13	8223.37	631.60	21.40	8036.51
Maize farming	I	–	–	–	–	–	–	–
	II	6540.73	13.34	2.78	7137.44	459.24	19.25	6324.39
Paddy farming	I	7817.65	16.43	3.07	7350.80	190.96	17.30	5244.73
	II	8507.17	12.58	2.39	7223.08	365.48	19.89	6391.57
Land Use	Group	Ag (µg/kg)	As (µg/kg)	Cd (µg/kg)	Ni (µg/kg)	Cu (µg/kg)	Hg (µg/kg)	Mo (µg/kg)
Conserved Area	I	38.58	1712.54	14.10	5497.25	4570.16	2.78	306.90
	II	69.99	1671.79	33.48	1965.92	1845.19	2.81	522.66
Maize farming	I	–	–	–	–	–	–	–
	II	18.81	1404.61	31.86	1577.48	1522.10	3.43	474.45
Paddy farming	I	37.18	1261.23	18.43	5160.29	4061.77	3.17	223.77
	II	36.82	1568.91	27.46	1957.94	1830.59	3.66	354.08

Note: in maize farming areas there was no group I type of schemes.

Table 3
The ratio of total PTEs with Tanzania and USEPA maximum allowable limit as an estimate of pollution hierarchy in land-use groups in Usangu basin-Tanzania.

Land Use	Group	AQ-Cr/TZ	AQ-Co/TZ	AQ-Fe/TZ	AQ-Mn/TZ	AQ-Zn/TZ	AQ-As/TZ
Conserved	I	0.18	3.41	1636.60	0.15	0.13	1.71
Area	II	0.15	4.13	1644.67	0.35	0.14	1.67
Maize	I	–	–	–	–	–	–
farming	II	0.14	2.99	1461.81	0.26	0.13	1.45
Paddy	I	0.16	3.07	1470.16	0.11	0.12	1.26
farming	II	0.126	2.39	1444.62	0.20	0.13	1.5
Land Use	**Group**	**AQ-Cd/TZ**	**AQ-Cu/TZ**	**AQ-Hg/TZ**	**AQ-Ni/TZ**	**AQ-Pb/TZ**	**AQ-Se/TZ**
Conserved	I	0.01	0.02	0.001	0.06	0.03	0.09
Area	II	0.03	0.01	0.001	0.02	0.04	0.19
Maize	I	–	–	–	–	–	–
farming	II	0.04	0.01	0.001	0.02	0.04	0.18
Paddy	I	0.02	0.02	0.002	0.05	0.03	0.11
farming	II	0.03	0.01	0.002	0.02	0.03	0.20
Land Use	**Group**	**AQ-Cr/USEPA**	**AQ-Co/USEPA**	**AQ-Fe/USEPA**	**AQ-Mn/USEPA**	**AQ-Zn/USEPA**	**AQ-As/USEPA**
Conserved	I	18.46	3.41	1636.59	53.88	3.82	8.56
Area	II	15.61	4.13	1644.67	126.32	4.28	8.35
Maize	I	–	–	–	–	–	–
farming	II	13.95	2.99	1461.81	91.70	3.91	7.28
Paddy	I	16.43	3.07	1470.16	38.19	3.46	6.31
farming	II	12.58	2.39	1444.62	73.09	3.98	7.85
Land Use	**Group**	**AQ-Cd/USEPA**	**AQ-Cu/USEPA**	**AQ-Hg/USEPA**	**AQ-Ni/USEPA**	**AQ-Pb/USEPA**	**AQ-Se/USEPA**
Conserved	I	0.14	2.29	0.56	0.11	55.41	0.09
Area	II	0.34	0.92	0.56	0.04	80.31	0.19
Maize	I	–	–	–	–	–	–
farming	II	0.36	0.77	0.57	0.03	71.29	0.18
Paddy	I	0.18	2.03	0.63	0.10	52.45	0.11
farming	II	0.28	0.96	0.73	0.04	63.92	0.20

3.3. The total PTEs spatial distribution in Usangu agro-ecosystem

The spatial distribution of total PTEs in different irrigation schemes (Group I and II) of Usangu agro-ecosystem, significantly varied ($P < 0.001$) among schemes and groups, where schemes located in the lowland areas (such as B and C in Fig. 2) had a significantly higher PTEs concentration ($P < 0.001$) such as Pb, Co, Cr, Fe, Cu, Ni, and Al than their counterparts (Table 4). This might be influenced by downstream runoffs from upland areas and soil erosion, but also the level of intensification which was observed to be high in these schemes (Ngailo et al., 2016). But also schemes located closer to urban or peri-urban areas or settlement areas (D and E in Group II of Fig. 2) were observed to have significantly higher mean PTEs values (such as Mn, Zn, Ag, As, Cd, Hg, Mo and Se) (Table 4). This can be due to runoffs, effluents and emission from urban areas and domestic wastes as supported by Shemdoe (2010). Furthermore, intensified and commercialized irrigation schemes were observed to have a higher PTEs concentration, which might increase production cost due to the unresponsive effect of fertilizer added due to nutrient fixation by PTEs (Wang et al., 2008) due to high agrochemicals use with reported high PTEs impurities.

Comparing irrigation scheme observed that areas in Group I such as Ilaji, Mabadaga, Kapunga, Mubuyuni and Uturo had a significantly higher concentration of Al, Cr, Fe, Co, Cu, Ni and Pb whilst scheme in Group II such as Chimala, Igalako, Ihahi and Mahongole had a high concentration of Mn, Zn, Ag, As, Cd, Hg, Mo and Se (Table 4). Based on Tanzania maximum allowable limit of PTEs in agricultural soils (Table 1); all irrigation schemes had a concentration of PTEs below Tanzania maximum allowable limit except for As, Ag, Mo, Co, and Fe which were above the TZ limits.Comparison of PTEs concentration with USEPA values observed that all ten irrigation schemes studied (Group I and II) had a concentration of Cr, Co, Fe, Mn, Zn, Ag, As, Cd, Cu, Mo and Pb above maximum allowable limit. Estimated AQ:TZ pollution hierarchy order among irrigation schemes in Usangu basin (Table 5) were Mabadaga>, Chimala>Uturo>Mubuyuni>Mahongole>Ilaji>Kapunga>Igalako>Ihahi >Isenyela (Table 5). The same trend was observed for AQ:USEPA. Based AQ:TZ computed ratio most schemes were less polluted with PTEs, however, in other hands when AQ:USEPA compared most schemes were observed to be polluted by many PTEs, this difference is due to regulatory values by these two authorities. This calls for special attention on the management of anthropogenic activ-

Table 4
The AQ mean values for PTEs concentrations in soils in paddy irrigation scheme in Usangu basin-Tanzania.

Scheme	Group	Al (mg/kg)		Cr (mg/kg)	Co (mg/kg)		Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	
Ilaji	I	8400.236		16.908	2.756		8355.306	331.282	17.914	
Isenyela	I	3414.048		5.801	1.034		4608.645	317.179	7.142	
Kapunga	I	9152.268		14.737	2.589		7050.136	178.997	18.642	
Mabadaga	I	13,793.938		34.236	6.432		10,523.858	236.902	20.956	
Mubuyuni	I	5426.666		18.246	3.661		7581.626	184.985	16.089	
Uturo	I	6375.796		19.55	3.869		8297.489	230.083	16.835	
Scheme	**Group**	**Al (mg/kg)**		**Cr (mg/kg)**	**Co (mg/kg)**		**Fe (mg/kg)**	**Mn (mg/kg)**	**Zn (mg/kg)**	
Chimala	II	7084.678		20.589	4.112		9073.318	238.692	20.624	
Igalako	II	7066.779		12.788	2.979		6808.079	348.424	17.729	
Ihahi	II	7354.573		11.302	1.83		6710.396	376.093	19.858	
Mahongole	II	10,201.698		14.718	3.29		8204.164	498.366	21.291	
Scheme	**Group**	**Ag (µg/kg)**	**As (µg/kg)**	**Cd (µg/kg)**	**Cu (µg/kg)**	**Hg (µg/kg)**	**Mo (µg/kg)**	**Ni (µg/kg)**	**Pb (µg/kg)**	**Se (µg/kg)**
Ilaji	I	65.426	1790.712	22.514	2772.961	1.082	331.278	3209.214	6094.816	2343.267
Isenyela	I	15.954	1061.84	17.786	392.694	2.258	392.264	380.515	4127.705	2038.427
Kapunga	I	42.39	1279.236	18.547	3487.318	3.1	260.851	4225.698	5469.322	2467.957
Mabadaga	I	9.861	869.284	35.548	7838.971	4.965	47.183	14,776.835	3888.987	1955.794
Mubuyuni	I	30.862	1259.914	16.774	5007.635	3.507	162.26	6513.476	5152.029	1475.085
Uturo	I	28.905	1452.661	13.488	5219.876	3.019	233.335	6107.45	4870.341	1695.849
Chimala	II	52.218	1606.015	16.707	5654.76	4.745	262.137	6821.882	5841.088	2143.628
Igalako	II	22.434	1327.771	35.244	1712.955	2.834	332.662	1750.769	6840.955	3028.077
Ihahi	II	31.304	1536.314	25.828	1591.123	3.652	417.295	1642.048	5959.581	4418.568
Mahongole	II	42.075	1700.945	34.068	1458.896	3.305	417.34	1521.588	7633.72	4123.352

Table 5
The ratio of total PTEs with Tanzania and USEPA maximum allowable limit of PTEs in agricultural soils as an estimate of pollution hierarchy in different irrigation schemes in Usangu basin-Tanzania.

Scheme	Group	AQ-Cr/TZ	AQ-Co/TZ	AQ-Fe/TZ	AQ-Mn/TZ	AQ-Zn/TZ	AQ-As/TZ	AQ-Cd/TZ	AQ-Cu/TZ	AQ-Hg/TZ	AQ-Ni/TZ	AQ-Pb/TZ	AQ-Se/TZ
Chimala	I	0.206	4.112	1814.664	0.133	0.137	1.61	0.017	0.028	0.002	0.068	0.029	0.107
Igalako	I	0.128	2.979	1361.616	0.194	0.118	1.32	0.035	0.009	0.001	0.018	0.034	0.151
Ihahi	I	0.113	1.83	1342.079	0.209	0.132	1.54	0.026	0.008	0.002	0.016	0.03	0.221
Ilaji	I	0.169	2.756	1671.061	0.184	0.119	1.79	0.023	0.014	0.001	0.032	0.03	0.117
Isenyela	I	0.058	1.034	921.729	0.176	0.048	1.06	0.018	0.002	0.001	0.004	0.021	0.102
Kapunga	I	0.147	2.589	1410.027	0.099	0.124	1.28	0.019	0.017	0.002	0.042	0.027	0.123
Mabadaga	II	0.342	6.432	2104.772	0.132	0.14	0.87	0.036	0.039	0.002	0.148	0.019	0.098
Mahongole	II	0.147	3.29	1640.833	0.277	0.142	1.70	0.034	0.007	0.002	0.015	0.038	0.206
Mubuyuni	II	0.182	3.661	1516.325	0.103	0.107	1.26	0.017	0.025	0.002	0.065	0.026	0.074
Uturo	II	0.195	3.869	1659.498	0.128	0.112	1.45	0.013	0.026	0.002	0.061	0.024	0.085
Scheme	Group	AQ-Cr/USEPA	AQ-Co/USEPA	AQ-Fe/USEPA	AQ-Mn/USEPA	AQ-Zn/USEPA	AQ-As/USEPA	AQ-Cd/USEPA	AQ-Cu/USEPA	AQ-Hg/USEPA	AQ-Ni/USEPA	AQ-Pb/USEPA	AQ-Se/USEPA
Chimala	I	20.589	4.112	1814.664	47.738	4.125	8.03	0.167	2.827	0.949	0.136	58.411	0.107
Igalako	I	12.788	2.979	1361.616	69.685	3.546	6.639	0.352	0.856	0.567	0.035	68.41	0.151
Ihahi	I	11.302	1.83	1342.079	75.219	3.972	7.682	0.258	0.796	0.73	0.033	59.596	0.221
Ilaji	I	16.908	2.756	1671.061	66.256	3.583	8.954	0.225	1.386	0.216	0.064	60.948	0.117
Isenyela	I	5.801	1.034	921.729	63.436	1.428	5.309	0.178	0.196	0.452	0.008	41.277	0.102
Kapunga	I	14.737	2.589	1410.027	35.799	3.728	6.396	0.185	1.744	0.62	0.085	54.693	0.123
Mabadaga	II	34.236	6.432	2104.772	47.38	4.191	4.346	0.355	3.919	0.993	0.296	38.89	0.098
Mahongole	II	14.718	3.29	1640.833	99.673	4.258	8.505	0.341	0.729	0.661	0.03	76.337	0.206
Mubuyuni	II	18.246	3.661	1516.325	36.997	3.218	6.3	0.168	2.504	0.701	0.13	51.52	0.074
Uturo	II	19.55	3.869	1659.498	46.017	3.367	7.263	0.135	2.61	0.604	0.122	48.703	0.085

ities which could contribute to higher PTEs levels in agricultural soils.

3.4. Bioavailable PTEs accumulation

The concentration of PTEs which are easily available for plant uptake in agro-ecosystem was determined by Mehlich 3 method (M3). The M3 mean values (mg/kg) for PTEs ranged Al (93.2–792.9), Cu (0.03–7.2), Fe (81.1–470.6), Mn (12.8503.1), Pb (0.03–4.8), and Zn (0.4–7.5). In addition, the concentration of other PTEs in agricultural soils (in µg/kg) ranged As (26.2–712.4), Cd (3.8–54.5), Co (45.2–2684.3), Cr (0.001–222.9), Hg (0.001–11.2), Ni (25.2–4497.3), and Se (97.2–4840.5). The bioavailable PTEs concentration determined were observed to be low compared to total PTEs determined by acid digestion. However, the determined values were enough to affect availability and uptake of plant nutrients such as phosphorus and environmental contamination (Malidareh et al., 2014). Rationing the M3 and AQ (M3:AQ) to estimate the percentage of total PTEs available for plant uptakes observed to range from 0.3 to 100% among studied PTEs. The high PTEs availability presents a risk since increased PTEs uptake by plants likely contaminate food chain or can easily be taken up by surface water runoffs to water resources posing health risks to soil invertebrates, animals and human (Fergusson and Ryan, 1984; Nriagu, 1992; Ordóñez et al., 2003). The overall trend for bioavailable PTEs distribution across irrigation schemes and land uses was observed to be significantly different among land uses groups and irrigation schemes, indicating the influence of natural and anthropogenic activities such as agrochemicals application and runoffs from semi-urbanized settlement available in farming areas. Many regulatory values for PTEs in agricultural soils and natural habitats are based on total metal concentrations. Therefore, consideration of bioavailable concentration can lower regulatory values allowing management action to be taken more early than the current values. Therefore, this study compared total and bioavailable PTEs to raise the concern to consider bioavailable PTEs concentration when establishing pollution and associated effects on soil invertebrates, plants, animals and human.

3.5. Land use and bioavailable PTEs (M3) distribution

Among the studied land use, the bioavailable PTEs were revealed to be significantly higher in farming areas (in paddy and maize farming areas) ($P < 0.05$) than in conserved areas (S1). This influenced by farming practices including the use of agrochemicals uses and storm runoff water for irrigation. The M3 PTEs distribution in different land uses was observed to vary among land uses and groups, where in each land use Group I had high concentration of bioavailable Al, Cu, Fe, Co, Cr, and Ni; while Group II reported high values of Mn, Pb, Zn, Ag, As, Cd, Hg, Mo and Se (S5). The M3 concentration of some PTEs in different land uses were: Pb in paddy farming (1.87 and 1.65 mg/kg for Group I and II), maize farming (1.87 mg/kg in Group II), and conserved area (1.82 and 2.02 mg/kg for Group I and II); As in paddy farming (190 and 270 µg/kg for Group I and II), maize farming (170 µg/kg for Group II), and conserved area (187 and 161 µg/kg for Group I and II); Cd in paddy farming (19 and 38 µg/kg for Group I and II), maize farming (33 µg/kg for Group II), and conserved area (17 and 36 µg/kg for Group I and II); and Co paddy farming recorded (844 and 474 µg/kg for Group I and II), Maize farming (532 µg/kg for Group II), and conserved area (685 and 634 µg/kg for Group I and II), these values were observed to be significantly different among land uses and groups ($P < 0.05$). The same trend of higher concentration of PTEs in paddy farming than other land use were observed in Mo, Ni and Se (S5), indicating the influence of anthropogenic activities as paddy farming in the study area is highly intensified. The comparison of available and total PTEs concentration (M3:AQ) in different land uses observed that there was a significant difference in availability among elements; elements with higher M3:AQ were Ag 11–100%, Cd 0–100%, Se 43–74%, Cu 48–64%, Mn 33–61.3%, Pb 25–38%, and other elements had percent availability (M3:AQ ratio) of less than 25% (S2). This indicates that the available PTEs high and likely to be taken up by plants and accumulate in food grains and fodders affecting human, animals and soil invertebrates.

3.6. Bioavailable PTEs spatial distribution in Usangu agroecosystem

The bioavailable PTEs distribution was observed to significantly to vary across schemes and groups (S3 and S5). For example; schemes in group I which composed of Ilaji, Isenyela, Kapunga, Mabadaga, Mubuyuni and Uturo had higher concentration of Al (199–346 mg/kg), Cu (0.3–4.2 mg/kg), As (86–468 µg/kg), Pb (0.64–2.74 mg/kg), Ag (0.2–33.12 µg/kg), Co (291–1619 µg/kg) and Ni (93.281–1770 µg/kg) while schemes in Group II (Chimala, Igalako, Ihahi, and Mahongole) had higher concentration of Se (0–2470.7 µg/kg), Hg (0–0.35 µg/kg), Cr (13.5–101.5 µg/kg), Cd (18.3–39.3 µg/kg), Zn (2.5–3.4 mg/kg), Fe (154–324 mg/kg) and Mn (118–227 mg/kg) (S3). The higher Al and Fe concentration has a toxicity effect on plants and reduce plant nutrients availability such as phosphorus due to fixation leading to poor fertilizer returns (Ndakidemi and Semoka, 2006). Higher PTEs concentration in Group I are likely to be influenced by intensive agricultural farming conducted in those areas which involved excessive use of fertilizer, pesticides and herbicides, and emission for machines and vehicles operating in agricultural fields. Group I schemes location favor it as a sink as it is located in the lower basin compared to Group II schemes; therefore, all storm surface runoffs from the upper Usangu basin flow to these schemes where they are utilized as irrigation water. Group II schemes being located in or near residential areas have an additional source of PTEs in agricultural soils from industrial and domestic waste, affecting PTEs concentration and distribution. Also, schemes in group II schemes are located closer to TAZAM highway and TAZARA diesel-powered railway line which might have influenced PTEs levels. Based on M3:AQ ratio estimated observed that the PTEs with high availability were Mn (27–81% in Group I and 42–67% in Group II), As (7–45% in Group I and 2–18% in Group II), Cd (4–100% in Group I and II), and Cu (12–44% in Group I and 40–54% in Group II) (S4). The variation of PTEs in schemes indicates that they are influenced by anthropogenic activities in farming areas and in proximity which are not uniformly distributed (S6). Therefore, PTEs management in agro-ecosystem needs integrated efforts to regulate agrochemicals and wastewater uses in agricultural fields but also waste disposal and storm runoffs management strategies has to be in place especially in urban and peri-urban areas.

4. Conclusion and way forward

Agricultural soils from the study area especially in farming areas for maize and paddy in the Usangu basin showed possible signs of Cd, Pb, Hg, As, Fe, Cu, Zn, and Hg contamination to a level, which can affect the soil invertebrates, animals, and human. The PTEs levels in agricultural soils in the study area were above Tanzania maximum allowable limits leading to possible health risks to the environment. The study found that Cd, Hg, and Pb in soils are related to land use activity and were negatively correlated with the altitude of the farming areas. Increased settlement and towns in farming areas were found to be associated with increased PTEs concentrations in soils because schemes located near residential areas had higher PTEs concentration. The study found that PTEs concentration increases with time and it is important to set management plans to monitor and control PTEs in agricultural soils to ensure environmental safety and sustainability.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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