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**Assessment of heavy metal contamination in agricultural soils
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Abstract

An investigation of possible pollution of heavy metals in the agriculture soils at Bani-Alharith, Sana'a, Yemen. was conducted using energy dispersive X-ray fluorescence spectrometry (EDXRF). Twenty soil samples (n=20) collected from the agriculture fields around Sana'a wastewater treatment plant were analyzed for heavy metals V, Cr, Co, Ni, Cu, Zn, Pb, Sn, Mn, Ti and Zr. The data revealed that the concentration levels of these heavy metals in all examined soil exceeded the recommended safety values as V (223 mg/kg) , Cr (365.5 mg/kg), Co (459 mg/kg), Ni (130 mg/kg), Cu (106.5 mg/kg), Zn (289 mg/kg), Pb (64 mg/kg), Sn (186.5 mg/kg), Mn (1437 mg/kg), Ti (12214 mg/kg) and Zr (657.5 mg/kg). Tin (Sn) and cobalt (Co) significantly exceeded recommended concentration limits. Soil contamination was assessed on the basis of contamination factor C_f^i , geoaccumulation index I_{geo} , and enrichment factor E_F . The mean C_f^i , I_{geo} and E_F decreased in the order of Sn > Co > Cr > Cu > Ni > Zn > V > Ti > Pb > Zr > Mn. The use of sewage water for irrigation could be one of the main reasons of high level of heavy metals in the studied area in addition to the anthropogenic activities and geogenic sources. A comprehensive environmental management strategy should be concerned by the government to address soil pollution in the agricultural areas, setting irrigation water quality standards and wastewater treatment plant management strategies.

Key Words: Heavy metal, contamination in agricultural soil, x-ray fluorescence spectrometry.

1. Introduction

Soils are complex mixtures of organic, inorganic materials and metal compounds from anthropogenic sources. It plays a key role in determining human well-being, providing key ecosystem services, supporting food production, and the natural recycling of C and essential nutrients in the environment. Soil is considered contaminated when chemicals are present or other alterations have been made to its natural environment. This is often originating from natural sources or different anthropogenic activities, such as mining, industrial activity, Sanitation (wastewater), accidental releases of chemicals or the improper disposal of hazardous waste [1, 2]. Moreover, inputs of heavy metals to soils through agricultural activities have increased in the past decades due to world population expansion [3]. Heavy metal content of soil is of major significance in relation to their fertility and nutrient status. Many metals such as Zn, Cu, and Se are essential elements for normal growth of plants and living organisms. However, high concentrations of these metals become toxic. Other metals, which are not included in the group of essential elements, such as Pb or Cr, may be tolerated by the ecosystem in low concentration, but become harmful in higher concentrations [4, 5]. The elevated levels of heavy metal in soil become one of the most serious pollutants in the natural environment due to their toxicity, persistence and ability to accumulate in soft tissues and enter the body via inhalation, ingestion, and skin absorption that whenever they accumulate in body tissue faster than the body's detoxification pathways, a gradual buildup of these toxins will occur.

In agricultural soils, the accumulation of heavy metals is a growing public concern because it threatens environmental health [6, 7] They can be accumulated in plants and animals, and then pass through the food chain and living organisms to human beings as the final consumer [8]. Conventional methods of soil analysis such as atomic absorption spectroscopy (AAS) [9], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [10] and inductively coupled plasma mass spectrometry (ICPMS) [11] involve soil sample preparation (which can include wet digestion). The methods are laborious, expensive and prone to inaccuracies due to the possibility of contamination from the chemical reagents used. Moreover, digestion often involves heating which may lead to loss of volatile analytes. More innovative analytical techniques are thus required for soil quality (SQ) analysis.

X-ray fluorescence (XRF) spectroscopy can be used as a potent tool which enables simultaneous quantitative analysis of the multi-elemental composition of samples [12]. The energy and intensity of the characteristic radiation of the element embedded are used to identify and quantify the concentration respectively. The analytical quality of the spectra obtained depends on the sample composition and instrumental parameters [13]. On the other hand, from a green analytical point of view, X-ray fluorescence (XRF) provides a reagent-free environmentally friendly and nondestructive technique, which permits to determine the mineral content of samples without any complex sample pre-treatment, thus minimizing laboratory space, resources and safety implications, also avoiding the use of chemical reagents. Furthermore, XRF presents the possibility of making in situ analysis and could be considered a green technique [14]. Thus, the XRF analysis is recommended for continuous monitoring a wide range of contamination sites.

Bani Al Harith is an agriculture area north Sanaa, the capital of Yemen. It is one of the main sources which provide many agricultural products to Sana'a. The main source of water used for irrigation in this area is the sewage water resulted from Sana'a wastewater treatment plant. The main problem is Sana'a treatment plant operator overloaded therefore the effluent is partially treated or sometimes untreated and the farmers used these effluents in agriculture. There is a real need to achieve investigation of some element concentrations in the agricultural soil, assess the spatial distribution of their anomalous locations, recognize the potential environmental risk and identify possible pollution sources in this area. According to the authors' knowledge, no study has previously performed comprehensive investigations in Bani Al Harith area to assess the heavy metal or trace elements and their impact on the agricultural soils. The aim of the present work is to study the potential soil contamination in Bani Al Harith agricultural area north Sana'a using Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRF) to identify the concentration of heavy metals and assess the contamination level in the agriculture soil. The results of this work may be helpful for the government in controlling and alleviating heavy metal contamination in the agricultural areas which will become a serious problem in the future, assist in developing strategies to wastewater treatment plant management and setting irrigation water quality standards.

2. Materials and methods

2.1 Description of the study area

The study area is "Bani Al-Hareth a district of the Sana'a Governorate, Yemen. Soil samples were collected from the agriculture fields around Sana'a wastewater treatment plant in the area located in 44°12'18" – 44°12'54" E longitude and 15°30'44.46"– 15°31'10.56" N latitude. The study area is bounded by Sana'a international airport from the south, Bait-Hanthal village from the west side. It is a plain wide-open area descending towards the north and it is free from hills and mountain areas.

The climate of the study area can be classified as arid. The ratio between average annual precipitation (P) and annual reference evaporation (Eo), (Arid $0.03 < P/Eo < 0,25$). The maximum temperature ranges between 29.5 ° in June and 22.2 ° in December and the minimum temperature ranges between 11.7 ° in August and 2.5 ° in December. The maximum value of humidity is 50% in April and November and the lowest value is 34% in June. The highest wind speed is 233 km/day in June. The sunshine hours are ranged between 8.9 hr in November and 6.3 hr in July. The rainy months are March, April and August with maximum rainfall reaches 68 in August. The studied area depends upon the sewage water in about 95% and only 5% from ground water to irrigate the cultivated areas. This refers to the high cost of wells water and decreased economical income in comparison to irrigation with sewer water (low cost) [15].

The major cultivated crops in the study area are:

1. Grains (50%) such as sorghum (both grain and fodder while roots and stems are used for fuel), barely (for feed and green fodder), wheat (Food crop), maize (fodder and fuel), pulses as lentil, fenugreek beans broad beans and chickpeas.
2. Vegetables (45%) such as potatoes, tomatoes, onion, cucumber...etc.
3. Fruit trees (5%).

2.2 Sampling and analysis

The effluent of Sana'a wastewater treatment plant is discharge through the open channel about 10 km to the end point near Arhab asphalt road. The soil samples were collected from the agriculture fields around Sana'a wastewater treatment plant along the two sides of the wastewater channel.

The location of the sampling points is shown in Fig. 1. Some agricultural crops in the study area and the open earth canal of the treated wastewater are shown in Fig 2 and 3.

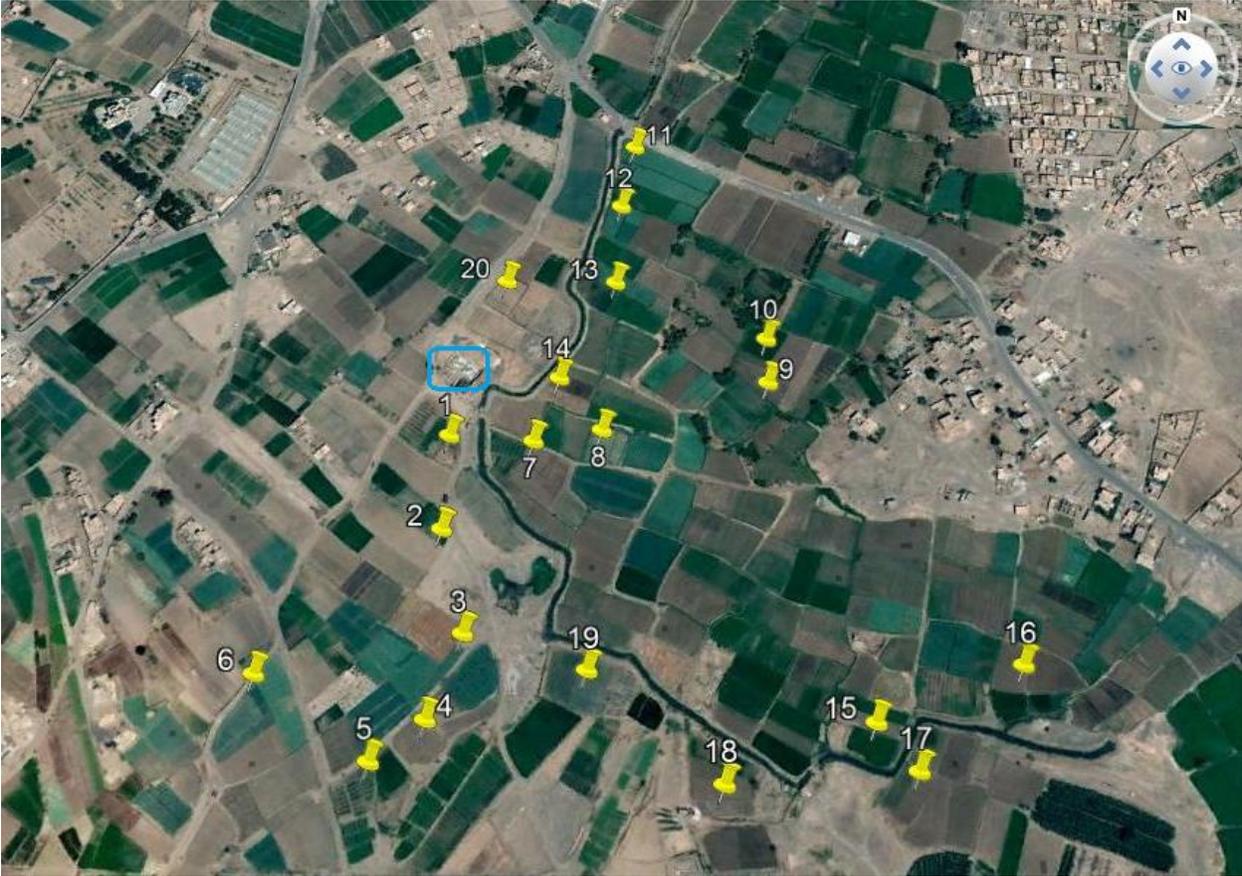


Fig. 1: Location of study area and distribution of sampling points. (the yellow points represent soil sampling sites, the blue region is the wastewater treatment plant and the black line is the wastewater channel).



Fig. 2: Some agricultural crops in the study area.



Fig. 3: The open earth canal of the treated wastewater.

20 soil samples were collected from the top soil (0-15cm) depth, which is usually contaminated. The exact longitude and latitude of the sampling sites has been determined were determined in the field through GPS Essentials program, based on the principles of Global Positioning System (GPS). The samples were removed from the large stones and plant materials and sealed in clean labeled polyethylene bags, kept in an isolated box and transported to the laboratory in the same day. In the laboratory, the soil samples were air dried at room temperature (25 °C) for a few days. The dry soil samples were finely powdered by swing-grinding mill and then sieved to 100 mesh size (US Standard). Sample pellets were prepared for analysis by Xray fluorescence spectrometry (XRF), using a hydraulic press and in collapsible aluminum cups.

4.0 g of each milled soil sample and 2.5 g of boric acid were added in the mold synchronously, and pressed into a 32 mm-diameter and pressed under a hydraulic press at 25-ton pressure to get a pellet (Hydraulic Press, specac, Ltd., UK).

2.3 Instrumentation

PANalytical Epsilon 3-XL Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRF) was used to determine the heavy metals in the soil samples. A Rhodium (Rh) anode is used in the X-

ray tube, which operated at up to 50 kV and current up to 3 mA; at a maximum power level of 15 W. The accuracy of the analysis was assessed by using standard reference samples.

2.4 Contamination assessment methods

2.4.1 Assessment of soil quality

In the interpretation of geochemical data, choice of background values plays an important role to compare trace element concentrations between contaminated and uncontaminated soils. Because of the background values of all elements of interest in the investigated soils are not known, metal concentrations in analyzed soils were compared with the Canadian Soil Quality Guidelines (Canadian Council of Ministers of the Environment, CCME, 2009) [16] to assess the pollution in the study area. Canadian Soil Quality Guidelines are defined as the concentrations recommended to provide a healthy, functioning ecosystem capable of sustaining the existing and likely future uses of the site by ecological receptors and humans.

2.4.2 The degree of contamination

The degree of contamination is expressed as:

- (1) Contamination factor (C_f^i),
- (2) Geoaccumulation index (I_{geo}), and
- (3) Enrichment factors (E_F)

All of these soil contamination indicators are calculated with respect to the concentration of elements in the Earth continental crust [17].

3. Results and discussion

3.1 Heavy metals concentrations:

XRF analyses of the soil samples identified the presence of metal oxides SiO₂, Al₂O₃, Fe₂O₃, CaO, K₂O, MgO, P₂O₅, Ti, Cl, Na₂O and SO₃ (major) and heavy metals V, Cr, Co, Ni, Cu, Zn, Pb, Sn, Mn, Ti and Zr (minor). The concentrations of these eleven heavy metals in all soil sampling sites

(n=20) were studied by XRF technique to assess their concentration levels in the studied agricultural soil.

Vanadium (V):

Vanadium content of soil depends upon the parent material and the pedogenic process associated with its development. Composition of the parent material has less bearing on V content of mature, developed soils. Vanadium usually has a wide and varied industrial usage in dyeing, textile, metallurgy and electronics. As majority of the industries are textile and petroleum products, which clearly indicates that the source is anthropogenic from industries in the area.

Chromium (Cr):

Chromium is a low mobility element, especially under moderately oxidizing and reducing conditions and near-neutral pH values. Cr^{6+} adsorption decreases with increasing pH, and Cr^{3+} adsorption increases with increasing pH. On the other hand, Cr (VI) is toxic for biological systems [18].

Cobalt (Co):

Co^{2+} belongs to a group of transition metals. It most often assumes the +2, +3, and less often a +1 oxidation state. Only the ^{59}Co isotope, representing 100 % of the isotopic composition of natural Co^{2+} is stable. Contamination of soils with Co^{2+} is mainly caused by mining and smelting activity, fertilizer use, and sewage sludge spreading. The bioavailability of Co^{2+} and, thus, its toxicity is also affected by the physicochemical properties of the soil environment such as structure, organic matter, pH, and complexing compounds. The response to an excess of Co^{2+} in a plant is heightened activity of superoxide dismutase (SOD), an enzyme responsible for O_2 dismutation and an increase in iron sequestration and ferritin synthesis. Co^{2+} plays a quite important role in the human body because it is the central atom of cobalamin, a coenzyme precursor, whose deficiency causes anemia [19].

Nickle (Ni):

Nickel is the 24th most abundant metal in the Earth's crust and 5th most abundant element by weight after iron, oxygen, magnesium and silicon, constituting about 3% of the earth composition. Nickel

usually exists in the 0 and +2 oxidation states, but less frequently in the -1, +1, +3 and +4 oxidation states. Naturally, nickel occurs widely in the environment, being released through both natural and anthropogenic sources, but seldom in its elemental form. Nickel's natural source to the environment include forest fires and vegetation, volcanic emissions and wind - blown dust. Industrial waste materials, lime, fertilizer and sewage sludge constitute the major sources of nickel into soils. Nickel from anthropogenic sources is more readily taken up by plants than that from natural occurring sources. The most common plants that have been identified for their tolerance to and hyper accumulation of nickel include cabbage, cauliflower and turnip as well as, leguminosae such as bean and pea. Food intake is the major route of nickel exposure for the general population [20].

Copper (Cu):

Copper occurs in the Earth's crust at concentrations between 25-75 mg kg⁻¹, with the abundance pattern that shows the tendency for the concentration in mafic igneous rocks (60-120 mg kg⁻¹) and argillaceous sediments (40-60 mg kg⁻¹), but it is rather excluded from the carbonate rocks (2-10 mg kg⁻¹). Copper can be released into the environment by both natural sources and human activities. It is often found near mines, industrial settings, landfills and waste disposals. In soil solids and solution copper occurs almost exclusively as the divalent cation Cu²⁺, and the reduction of Cu²⁺ to Cu⁺ and Cu⁰ is possible under reducing conditions. The most important sink for Cu is soil organic matter, and its complexation with organic matter. Copper is retained in soils through exchange and specific adsorption mechanisms. High dose of Copper is said to be toxic and carcinogenic. Overdoses of copper may also lead to neurological complications, hypertension, liver and kidney dysfunctions [21].

Zinc (Zn):

Zinc belongs to a group of trace metals, which are essential for the growth of humans, animals and plants and are potentially dangerous for the biosphere when present in high concentrations. The main sources of pollution are industries and the use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides in agriculture [22]. Higher contamination of zinc causes hematological disorders.

Lead (Pb):

The species of Pb vary considerably with soil type; it is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. In some soil types, Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations. Lead is released from smelting, motor-vehicle exhaust fumes, chemical fertilizer and from corrosion of lead pipe work. Lead solubility is controlled principally by PbCO_3 and low-alkalinity and low-pH waters can have higher Pb concentrations. The presence of lead reduces the enzymatic activity of the biota, and in consequence, incompletely decomposed organic material accumulates in the soil [23].

Tin (Sn):

Tin (Sn) is a naturally occurring heavy metal in the Earth's crust, at an average concentration of 2.5 mg/kg. It is therefore also a component of many soils due to the natural weathering of bedrock. It is found in two oxidative states, stannous (+2) and stannic (+4). The concentration of Sn in the environment is highly variable, and is dependent on the use and release of Sn containing products by both natural sources such as the weathering of rocks and volcanic eruptions, and anthropogenic activities such as industrial processes, agriculture and mining. In the soil, Sn usually has limited to no mobility, and is usually tightly bound in the top soil. The effects of soil Sn^{2+} mobility should be examined. When the concentrations of Sn in soil increase, the amount of Sn supplied to the plants also increases and higher concentrations will be taken up and incorporated into the plant tissues [24].

Manganese (Mn):

Manganese is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. Manganese occurs principally as pyrolusite (MnO_2), and to a lesser extent as rhodochrosite (MnCO_3). Manganese is one of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leaves and brown spots on leaves. The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. The foodstuffs that contain the highest concentrations are grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. After absorption in the human body manganese will

be transported through the blood to the liver, the kidneys, the pancreas and the endocrine glands [25].

Titanium (Ti):

Titanium (Ti) is the ninth most abundant element in the earth's crust and makes up about 0.25% by moles and 0.57% by weight of the crust. Ti is the second most abundant transition metal, after iron (Fe). Ti exhibits oxidation states of Ti^{2+} , Ti^{3+} (titanous), and Ti^{4+} (titanic), of which Ti^{2+} and Ti^{3+} are unstable, while Ti^{4+} is the most stable ion. The most important compound is TiO_2 , which is mainly used in paints. Although Ti is not toxic for animals and humans, its effects on plants and bacteria show noteworthy concentration dependence. For plants, it shows beneficial effects on various physiological parameters at low doses and is toxic at higher ones. Although Ti is beneficial, it is not essential: Ti deficiency does not exist [26].

Zirconium (Zr):

Zr is the twentieth most common element in the earth's crust. It is generally considered to be immobile in soil because it has low water solubility and a strong tendency to polymerize. Moreover, Zr forms strong complexes with soil components, via zirconium dioxide and zirconocene dichloride, among others. The rate of adsorption/desorption of Zr to soil depends on its speciation and the characteristics of the soil involved. This element can be mobile in soil under a wide range of geological settings such as tropical weathering. Anthropogenic activities can modify the amount and nature of Zr that is present in soils and should be considered as a possible soil pollutant. Zr can significantly reduce plant growth and can affect plant enzyme activity.

The concentrations of the heavy metals V, Cr, Co, Ni, Cu, Zn, Pb, Sn, Mn, Ti and Zr were identified using XRF spectroscopy and their levels in the soil at various sampling points are presented in Table 1.

Table 1: Heavy metal concentration (mg/kg) in soil samples-XRF data.

Sample No.	V	Cr	CO	Ni	Cu	Zn	Pb	Sn	Mn	Ti	Zr
1	250	410	430	100	100	330	70	190	1110	14540	710
2	210	510	350	100	70	160	50	160	1070	11570	620
3	250	350	460	110	90	270	60	200	1220	15960	820
4	260	440	460	140	130	340	60	210	1580	13800	890
5	270	350	440	120	90	230	50	----	1310	14460	720
6	270	400	420	130	90	200	50	200	1290	13370	660
7	160	280	490	110	80	210	50	140	1310	9160	490
8	190	350	400	140	100	260	60	180	1470	10540	540
9	190	260	420	130	170	480	90	160	1410	10780	570
10	210	420	430	130	110	300	70	210	1560	10490	640
11	210	300	430	140	110	290	70	170	1530	11990	700
12	230	470	470	140	130	360	70	220	1380	13320	760
13	250	450	500	140	110	360	70	----	1420	13450	770
14	190	310	440	140	110	340	70	190	1500	10720	590
15	230	320	470	140	130	360	80	190	1480	12010	580
16	230	280	450	140	140	410	80	190	1600	12040	640
17	200	320	730	120	80	180	50	160	1480	10800	560
18	200	310	430	140	90	220	60	170	1540	11090	550
19	230	320	500	160	110	290	70	----	1760	11790	640
20	230	460	460	130	90	190	50	230	1730	12410	700

Descriptive statistics (minimum value, maximum value, mean, median and standard deviation SD) of the analyzed samples for the elements and reference value of metal concentrations in the upper continental crust are tabulated in Table 2.

Table 2: Statistics of the determined elements in soil samples, and reference value of element concentrations in Canadian Soil Quality Guidelines Ref. [16] and in the upper continental crust Ref. [17].

	V	Cr	CO	Ni	Cu	Zn	Pb	Sn	Mn	Ti	Zr
minimum	160	260	350	100	70	160	50	140	1070	9160	490
maximum	270	510	730	160	170	480	90	230	1760	15960	890
mean	223	366	459	130	107	289	64	186.47	1437.5	12214.5	657.5
median	230	350	445	135	105	290	65	190	1475	12000	640
S D	29.93	73.52	72.76	15.56	24.12	84.35	11.88	24.22	181.68	1693.60	101.92
Ref [16]	130	64	40	50	63	200	70	5	-----	-----	-----
Ref [17]	53	35	11.6	18.6	14.3	52	17	2.5	527	3117	237

The data revealed that the mean concentrations of heavy metals were significantly high for all elements. The heavy metals with enrichment levels exceeding the normally expected distribution in soil give rise to concern over the suitability of soils for growing crops.

Comparing the mean concentration value of each element in the examined soil sites (n=20) with the values recommended by Canadian Soil Quality Guidelines (CCM) [16] and the concentration value of element in the upper continental crust [17] reveals that contaminants can be arranged in descending order as follows; Sn > Co > Cr > Cu > Ni > Zn > V > Ti > Pb > Zr > Mn. Table 2 shows that the soils of the study area are enriched in relation to values recommended by CCM with factors of 37 for Sn; 11.5 for Co; 5.7 for Cr; 2.6 for Ni; 1.7 for V; 8.16 for Zn and cu; 1.4 for Zn and 0.9 for Pb. The mean values of Mn, Ti and Zr are about 2.7, 3.9 and 2.8 respectively times the natural background values in the upper continental crust.

The elevated concentrations of Sn, Co, Cr, Cu, Ni, Zn, V, Ti, Pb, Zr and Mn in the examined soil suggested anthropogenic sources of these elements.

3.2 Contamination factor (C_f^i)

It is used to describe the contamination of a given toxic element and assess the soil contamination. According to Hakanson and Liu *et al.* [27,28], C_f^i was calculated using the following equation:

$$C_f^i = \frac{C_{0-1}}{C_n^i} \quad (1)$$

where C_{0-1}^i refers to mean concentration of each element in soil and C_n^i refers to baseline or background value. The concentration of elements in the Earth's crust were used as a reference value, similar to the other factors. The calculated values of contamination factor for the determined heavy elements in soil samples are tabulated in Table 3 and the degree of contamination by metals according to soil index, contamination factor is listed in Table 4.

Table 3 : Results of contamination factor C_f^i for the determined heavy elements in soil samples.

Sample No.	V	Cr	CO	Ni	Cu	Zn	Pb	Sn	Mn	Ti	Zr
1	4.72	11.71	37.07	5.38	6.99	6.35	4.12	76.00	2.11	4.66	3.00
2	3.96	14.57	30.17	5.38	4.90	3.08	2.94	64.00	2.03	3.71	2.62
3	4.72	10.00	39.66	5.91	6.29	5.19	3.53	80.00	2.31	5.12	3.46
4	4.91	12.57	39.66	7.53	9.09	6.54	3.53	84.00	3.00	4.43	3.76
5	5.09	10.00	37.93	6.45	6.29	4.42	2.94		2.49	4.64	3.04
6	5.09	11.43	36.21	6.99	6.29	3.85	2.94	80.00	2.45	4.29	2.78
7	3.02	8.00	42.24	5.91	5.59	4.04	2.94	56.00	2.49	2.94	2.07
8	3.58	10.00	34.48	7.53	6.99	5.00	3.53	72.00	2.79	3.38	2.28
9	3.58	7.43	36.21	6.99	11.89	9.23	5.29	64.00	2.68	3.46	2.41
10	3.96	12.00	37.07	6.99	7.69	5.77	4.12	84.00	2.96	3.37	2.70
11	3.96	8.57	37.07	7.53	7.69	5.58	4.12	68.00	2.90	3.85	2.95
12	4.34	13.43	40.52	7.53	9.09	6.92	4.12	88.00	2.62	4.27	3.21
13	4.72	12.86	43.10	7.53	7.69	6.92	4.12		2.69	4.32	3.25
14	3.58	8.86	37.93	7.53	7.69	6.54	4.12	76.00	2.85	3.44	2.49
15	4.34	9.14	40.52	7.53	9.09	6.92	4.71	76.00	2.81	3.85	2.45
16	4.34	8.00	38.79	7.53	9.79	7.88	4.71	76.00	3.04	3.86	2.70
17	3.77	9.14	62.93	6.45	5.59	3.46	2.94	64.00	2.81	3.46	2.36
18	3.77	8.86	37.07	7.53	6.29	4.23	3.53	68.00	2.92	3.56	2.32
19	4.34	9.14	43.10	8.60	7.69	5.58	4.12		3.34	3.78	2.70
20	4.34	13.14	39.66	6.99	6.29	3.65	2.94	92.00	3.28	3.98	2.95
mean	4.21	10.44	39.57	6.99	7.45	5.56	3.76	74.59	2.73	3.92	2.77
S D	0.56	2.10	6.27	0.84	1.69	1.62	0.70	9.69	0.34	0.54	0.43

Table 4 : Degree of contamination by metals according to soil index, Contamination factor (C_f^i).

Index	Value	Degree of contamination
C_f^i	< 1	low contamination;
	1 - 3	moderate contamination;
	3 - 6	considerable contamination;
	≥ 6	very high contamination.

Mean and standard deviation (S D) values of soil contamination indicators are presented in Table 3. The results showed that the elements Sn (74.59), Co (39.57), Cr (10.44), Cu (7.45) and Ni (6.99) fall in class of very high contamination while V (4.21), Zn (5.56), Ti (3.92) and Pb (3.76) are in class of considerable contamination. Only Mn (2.73) and Zr (2.77) showed moderate level of contamination factor.

3.3 Geoaccumulation index (I_{geo})

According to Muller [29], I_{geo} was applied to quantify the elemental pollution in soils and assess their related degree. It could be calculated using Müller's equation as follows:

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5 B_n} \right] \quad (2)$$

where C_n is the measured concentration of an element in the soil, B_n is the geochemical background of an element (n), and the constant 1.5 is the background matrix correction factor due to lithogenic effects. Table 5 lists the results of geoaccumulation index (I_{geo}), the mean and S D for the determined heavy elements in soil samples. Degree of contamination by metals according to geoaccumulation soil index (I_{geo}) is listed in Table 6.

Table 5 : Results of geoaccumulation indices (I_{geo}) for the determined heavy elements in soil samples.

Sample No.	V	Cr	CO	Ni	Cu	Zn	Pb	Sn	Mn	Ti	Zr
1	1.65	2.97	4.63	1.84	2.22	2.08	1.46	5.66	0.49	1.64	1.00
2	1.40	3.28	4.33	1.84	1.71	1.04	0.97	5.42	0.44	1.31	0.80
3	1.65	2.74	4.72	1.98	2.07	1.79	1.23	5.74	0.63	1.77	1.21
4	1.71	3.07	4.72	2.33	2.60	2.12	1.23	5.81	1.00	1.56	1.32
5	1.76	2.74	4.66	2.10	2.07	1.56	0.97		0.73	1.63	1.02
6	1.76	2.93	4.59	2.22	2.07	1.36	0.97	5.74	0.71	1.52	0.89
7	1.01	2.42	4.82	1.98	1.90	1.43	0.97	5.22	0.73	0.97	0.46
8	1.26	2.74	4.52	2.33	2.22	1.74	1.23	5.58	0.89	1.17	0.60
9	1.26	2.31	4.59	2.22	2.99	2.62	1.82	5.42	0.83	1.21	0.68
10	1.40	3.00	4.63	2.22	2.36	1.94	1.46	5.81	0.98	1.17	0.85
11	1.40	2.51	4.63	2.33	2.36	1.89	1.46	5.50	0.95	1.36	0.98
12	1.53	3.16	4.76	2.33	2.60	2.21	1.46	5.87	0.80	1.51	1.10
13	1.65	3.10	4.84	2.33	2.36	2.21	1.46		0.85	1.52	1.12
14	1.26	2.56	4.66	2.33	2.36	2.12	1.46	5.66	0.92	1.20	0.73
15	1.53	2.61	4.76	2.33	2.60	2.21	1.65	5.66	0.90	1.36	0.71
16	1.53	2.42	4.69	2.33	2.71	2.39	1.65	5.66	1.02	1.36	0.85
17	1.33	2.61	5.39	2.10	1.90	1.21	0.97	5.42	0.90	1.21	0.66
18	1.33	2.56	4.63	2.33	2.07	1.50	1.23	5.50	0.96	1.25	0.63
19	1.53	2.61	4.84	2.52	2.36	1.89	1.46		1.15	1.33	0.85
20	1.53	3.13	4.72	2.22	2.07	1.28	0.97	5.94	1.13	1.41	0.98
mean	1.48	2.77	4.71	2.21	2.28	1.83	1.30	5.62	0.85	1.37	0.87
S D	0.20	0.29	0.20	0.18	0.31	0.43	0.27	0.19	0.19	0.20	0.22

Table 6 : Degree of contamination by metals according to geoaccumulation soil index (I_{geo}).

Index	Value	Degree of contamination
I_{geo}	< 1	Uncontaminated
	0-1	Uncontaminated-Moderate
	1 - 2	Moderate
	2 - 3	Moderate-Strong
	3 - 4	Strong
	4 - 5	Strong-very strong
	> 5	Very strong

Comparing the mean values of geoaccumulation factor listed in Table 5 with the degree of contamination classified in Table 6, one can see that the I_{geo} Index of Sn and Co are in the very strong and Strong-very strong contaminated level respectively. The I_{geo} Index of Cr, Ni and Cu fall in moderate-strong category while V, Zn, Pb and Ti show moderate level of I_{geo} Index. The geoaccumulation index of Mn and Zr is in the range between 0-1 which reveals uncontaminated to moderate contamination level.

3.4 Enrichment factors (E_F)

It can be applied to determine whether the surface layers of soils are enriched in trace elements compared with an uncontaminated reference material [30], quantify significant heavy metal inputs above natural levels [31] and evaluate the anthropogenic contribution to the trace metal content in the composite soil collection [32]. The E_F was based on the standardization of a tested element against a reference one such as Aluminum (Al) or Iron (Fe). The E_F calculation was expressed as follows:

$$E_F = [C_X/C_{Ref}]_{sample} / [C_X/C_{Ref}]_{background} \quad (3)$$

where C_x is the concentration of the element of interest and C_{Ref} is the concentration of reference element for normalization. In this work, Aluminum concentration was used to calculate E_F . A reference element is the one characterized by low occurrence variability. In this study Aluminum was used as reference element due to its low occurrence. Al is one of the main components of the Earth's crust and its concentration in soil is also connected with some matrix.

Table 7 : Results of Enrichment Factor (E_F) for the determined elements in soil samples.

Sample No.	V	Cr	CO	Ni	Cu	Zn	Pb	Sn	Mn	Ti	Zr
1	4.31	10.70	33.86	4.91	6.39	5.80	3.76	69.42	1.92	4.26	2.74
2	3.86	14.18	29.36	5.23	4.76	2.99	2.86	62.28	1.98	3.61	2.55
3	4.65	9.86	39.10	5.83	6.21	5.12	3.48	78.88	2.28	5.05	3.41
4	4.96	12.72	40.12	7.62	9.20	6.62	3.57	84.99	3.03	4.48	3.80
5	5.12	10.05	38.12	6.48	6.33	4.45	2.96	0.00	2.50	4.66	3.05
6	5.11	11.46	36.31	7.01	6.31	3.86	2.95	80.23	2.45	4.30	2.79
7	2.55	6.76	35.71	5.00	4.73	3.41	2.49	47.34	2.10	2.48	1.75
8	3.18	8.87	30.57	6.67	6.20	4.43	3.13	63.83	2.47	3.00	2.02
9	3.00	6.22	30.34	5.86	9.96	7.73	4.44	53.62	2.24	2.90	2.02
10	3.73	11.29	34.89	6.58	7.24	5.43	3.88	79.05	2.79	3.17	2.54
11	3.50	7.57	32.75	6.65	6.80	4.93	3.64	60.08	2.57	3.40	2.61
12	4.18	12.93	39.03	7.25	8.76	6.67	3.97	84.76	2.52	4.12	3.09
13	4.57	12.46	41.78	7.30	7.46	6.71	3.99	0.00	2.61	4.18	3.15
14	3.14	7.77	33.26	6.60	6.74	5.73	3.61	66.63	2.50	3.02	2.18
15	3.73	7.87	34.87	6.48	7.82	5.96	4.05	65.40	2.42	3.32	2.11
16	3.78	6.97	33.78	6.55	8.53	6.87	4.10	66.18	2.64	3.36	2.35
17	3.41	8.26	56.83	5.83	5.05	3.13	2.66	57.79	2.54	3.13	2.13
18	3.25	7.62	31.90	6.48	5.42	3.64	3.04	58.51	2.51	3.06	2.00
19	3.93	8.28	39.05	7.79	6.97	5.05	3.73	0.00	3.03	3.43	2.45
20	4.12	12.49	37.68	6.64	5.98	3.47	2.79	87.42	3.12	3.78	2.81
mean	3.90	9.72	36.47	6.44	6.84	5.10	3.45	58.32	2.51	3.64	2.58
S D	0.73	2.41	5.93	0.80	1.44	1.41	0.55	27.42	0.32	0.68	0.53

Table 8 : Degree of contamination by metals according to soil index, Enrichment Factor (E_F).

Index	Value	Degree of contamination
E_F	1.1 - 2	Slight
	2.1 - 4	Moderate
	4.1 - 8	Severe
	8.1 - 16	Very severe
	> 16	Excessive

The Enrichment factor (E_f) values calculation results listed in Table 7 show that the investigated agricultural soil can be assessed to be excessive polluted with Sn and Co, very severe polluted with Cr, severe polluted with Ni, Cu and Zn, moderate polluted with V, Pb, Mn, Ti and Zr.

4. Conclusion

This study shows that concentrations of V, Cr, Co, Ni, Cu, Zn, Pb, Sn, Mn, Ti and Zr exceeded recommended limits in the agricultural soil and their background concentration in the Earth's continental crust by factors of 37 for Sn; 11.5 for Co; 5.7 for Cr; 2.6 for Ni; 1.7 for V; 8.16 for Zn and Cu; 1.4 for Zn and 0.9 for Pb. Tin (Sn) and cobalt (Co) showed significantly high concentration limits. The contamination factor showed that all soil samples were in the very high- considerable moderate and moderate contaminated categories. The Igeo Index showed that most of the samples sites were classified as moderately contaminated. Sn and Co were strong-very strong contaminated while Mn and Zr were uncontaminated-moderate level. The EF decreased in the order of Sn > Co > Cr > Cu > Ni > Zn > V > Ti > Pb > Zr > Mn, indicating that the study areas were severely contaminated with Sn and Co. High concentration of these toxic elements in soil is responsible for the development of toxicity in agriculture products, which in turn affects human life. In addition to the anthropogenic activities and geogenic sources, sewage water which used for irrigation could be one of the main reasons of high level of heavy metals in the studied area. The government should manage strategies to address soil pollution in the agricultural areas, setting irrigation water quality standards and wastewater treatment plant management.

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References

- [1] R. H. Merry, Tiller, K.G., Distribution and budget of cadmium and lead in an agricultural region near Adelaide, South Australia. *Water Air Soil Pollut.* 57/58 (1991) 171–180.
- [2] S. Khan, Q. Cao, Y.M. Zheng, Y.Z. Huang, Zhu, Y.G., 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environ. Pollut.* 152, 686-692.
- [3] Y. Li, X. Gou, G. Wang, Q. Zhang, Q. Su, G. Xiao, Heavy metal contamination and source in arid agricultural soil in central Gansu Province, China, *J. Environ. Sci.* 20 (2008) 607–612
- [4] B.J. Alloway, D.C. Ayres, *Chemical Principles of Environmental Pollution*, second edition, Blackie Academic and Professional, Chapman and Hall, London, 1997, pp 208–211.
- [5] J.O. Nriagu, Production and uses of chromium, in: J.O. Nriagu, E. Niebner (Eds.), *Chromium in the Natural and Human Environments*, Wiley, New York, 1988, pp. 81–104.
- [6] M. Harmanescu, L.M. Alda, D.M. Bordean, I. Gogoasa, I. Gergen, Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; a case study: Banat County, Romania. *Chem. Central J.* 5, (2011) 64-64.
- [7] Q. Wu, J.Y.S. Leung, X. Geng, S. Chen, X. Huang, H. Li, Z. Huang, L. Zhu, J. Chen, Y. Lu, Heavy metal contamination of soil and water in the vicinity of an abandoned e-waste recycling site: implications for dissemination of heavy metals. *Sci Total Environ.*, 15;506-507 (2015) 217-25.
- [8] L.P. Cui, J.F. Bai, Y.H. Shi, S.L. Yan, W.H. Huang, X.Y. Tang, Heavy metals in soil contaminated by coal mining activity. *Acta Pedol. Sin.* 41 (6), (2004) 896-904 (in Chinese).
- [9] J. Wang, E.H. Hansen, Trends and perspectives of flow injection/sequential injection on-line sample-pretreatments schemes coupled to ETAAS, *TRACTrends Anal. Chem.* 24 (2005) 1–8.
- [10] D.J. Butcher, Advances in inductively coupled plasma optical emission spectrometry for environmental analysis, *Instrum. Sci. Technol.* 38 (2010) 458–469
- [11] N.J. Miller Ihli, S.A. Baker, Trace element composition of municipal waters in the United States: a comparison of ICP-AES and ICP-MS methods, *J. Food Compos. Anal.* 14 (2006) 619–629
- [12] D.J. Kalnicky, R. Singhvi, Field portable XRF analysis of environmental samples, *J. Hazard. Mater.* 83 (2001) 93–122.
- [13] K. Tsuji, K. Nakano, H. Hayashi, K. Hayashi, C.U. Ro, *Anal. Chem.* 80 (12) (2008) 4421–4454.
- [14] S. Armenta, S. Garrigues, M. de la Guardia, *Trends Anal. Chem.* 27 (2008) 497.
- [15] PACER Consultants. (2006), *Studies & Design the Reuse of Wastewater from Sana'a Wastewater Treatment Plant.*
- [16] Canadian Council of Ministers of the Environment, 2009. *Canadian Soil Quality Guidelines for the - Protection of Environmental and Human Health, Summary Tables.*
- [17] K. Hans Wedepohl, The composition of the continental crust, *Geochimica et Cosmochimica Acta*, Vol. 59, No. 7, (1995) 1217-1232,
- [18] Kabata-Pendias, *Trace Elements in Soils and Plants* (3rd ed.), CRC Press, Boca Raton, FL, 2001.

- [19] Magdalena Zaborowska & Jan Kucharski & Jadwiga Wyszowska, Biological activity of soil contaminated with cobalt, tin, and molybdenum, *Environ Monit Assess* 188: 398 (2016).
- [20] Yahaya Ahmed Iyaka, Nickel in soils: A review of its distribution and impacts, *Scientific Research and Essays Vol. 6(33)*, (2011) 6774-6777.
- [21] Larocque ACL, Rasmussen PE (1998) An overview of trace metals in the environment: mobilization to remediation. *Environ Geology* 33:85–91
- [22] M. Romic, D. Romic, Heavy metal distribution in agricultural top soils in urban area, *Environ. Geol.* 43 (2003) 795–805.
- [23] C.S.C. Wong, X.D. Li, Pb contamination and isotopic composition of urban soils in Hong Kong, *Sci. Total Environ.* 319 (2004) 185–195.
- [24] Muller FL, LF Cyster, LM Raitt, J Aalbers, The effects of tin (Sn) additions on the growth of spinach plants, *FYTON* (2015) 84: 461-465
- [25] <https://www.lenntech.com/periodic/elements/mn.htm#ixzz6FuGu5MBr>
- [26] Lyu S, Wei X, Chen J, Wang C, Wang X and Pan D, Titanium as a Beneficial Element for Crop Production. *Front. Plant Sci.* 8:597 (2017).
- [27] L. Hakanson, An ecological risk index for aquatic pollution control. A sedimentological approach, *Water Res.* 14 (1980) 975–1001.
- [28] W.H. Liu, J.Z. Zhao, Z.Y. Ouyang, L. Soderlund, G.H. Liu, Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. *Environ. Int.* 31, (2005) 805-812.
- [29] G. Muller, Index of geoaccumulation in sediments of the Rhine River, *J. Geol.* 2 (1969) 108–118.
- [30] Nguessan, Y.M., Probst, J.L., Bur, T., Probst, A., Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France), *Sci. Total Environ.*, 407, (2009) 2939-2952.
- [31] Birch, G., Siaka, M., Owens, C., The source of anthropogenic heavy metals in fluvial sediments of a rural catchment: Coxs river, Australia. *Water Air Soil Pollut.* 126, (2001) 13-35.
- [32] Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Sci. Total Environ.* 312, (2003) 195-219.