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Research Paper

Monitoring And Determination of Heavy Metals as Pollutants in Tomato Agricultural Greenhouse Soils at Zilfi Province

Chemistry

KEYWORDS : green house, Zilfi, Heavy metals and ICP-MS

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ABSTRACT

Determination of nine heavy metals(Cr, Ni, Cd, Co, Hg, Zn, As, Pb, and Cu) as pollutants in agricultural soil of ten farms in greenhouse conditions at Zilfi Province –Saudi Arabia, was carried out using ICP-MS (Inductively Coupled Plasma-Mass Spectrometer).The study found that soil samples are not contaminated with five elements :Ni, Co, Hg, Zn, and Cu .The concentrations of the rest elements(Cr, Cd, As, and Pb) were more than the maximum permitted values of WHO for soils .The maximum concentrations for these elements are as follows: Cr(333.4 gm/kg),Cd(85 gm/kg), As(38.8 mg/kg) and Pb(160.2 mg/kg).

INTRODUCTION

Heavy metal contamination of food is one of the most important aspects of food safety and quality assurance[Sharma ,Agrawal and Marshall 2009]. Vegetables represent a rich source of vitamins, minerals, and fibers for human diet, and they also have beneficial antioxidative effects. However, vegetables grown in contaminated soils can accumulate relatively high amounts of heavy metals [Sharma, et al. 2006. and Marshall, Holden , Ghose, Chisala, Kapungwe., Volk, Agrawal, Agrawal, Sharma., and Singh.2007].

Excessive accumulation of heavy metals in agricultural land may result in soil contamination and increased heavy metal uptake by crops, leading to deleterious effects on food quality and safety[Garcia. and Millan 1998]. Food chain contamination is one of the important pathways for the entry of these toxic metals into the human body[Ma., Hung , and Chen 2006]. Therefore, dietary intake of heavy metal through contaminated vegetables may pose health risk to humans[Singh, Sharma., Agrawal and Marshall 2010.].

The level of nutrients, heavy metals present in small ammounts, absorbed by plants is related to their bioavailiability in the growth medium. Meanwhile, uptake of nutrients increases for some nutrients or decreases for the others depending on antagonistic or synergistic (interactions) effects among plant minerals and other nutrients [Yildiz, 2005].

Vegetables accumulate heavy metals in their edible and non edible parts. Although some of the heavy metals such as Zn, Mn, Ni and Cu act as micro-nutrients at lower concentrations, they become toxic at higher concentrations. Health risk due to heavy metal contamination of soil has been widely reported[Scrimshaw and Lester. 2006, and Anita, Sharma, Agrawali, and, Marshall 2010]. Consumption of these vegetables with elevated levels of heavy metals may lead to high level of body accumulation causing related health disorders. Thus regular monitoring of heavy metal contamination in the vegetables grown at area, such as close to industry, suspicious soils, and of course in greenhouse, is necessary, and of course the consumption of contaminated vegetables should be avoided in order to reduce the health risk caused by taking the contaminated vegetables .

This food chain contamination is one of the important pathways for the entry of these toxic pollutants into the human body. Heavy metal accumulation in plant depend upon plant species and the efficiency of different plants depends is evaluated by either plant uptake or soil to plant transfer factors of the metal.[Rattan, Dattan, Chhonkar,. Suribabu and Singh 2005].

Vegetables take up metals by absorbing them from contaminated soil as well as from deposits on different parts of the vegetables exposed to the air from polluted environments [Sobukola,. Adeniran, , Odedairo and Kajihausa 2003]. Vegetable plants growing on heavy metal contaminated medium can accumulate high concentrations of trace elements to cause serious health risk to consumers[Long, Yang, Ye, He, Calvert and Stoffella, 2010]. Trace quantities of certain heavy elements, such as chromium, cobalt, copper, manganese and zinc are essential micronutrients for higher animals and for plant growth.[Somers, 1974]. Lead (Pb), cadmium (Cd), and nickel (Ni) are significant environmental pollutants. Anthropogenic activities, such as agriculture, industry and urban life increase the Pb, Cd, and Ni contents of soils and waters and, therefore, have an effect on the metal contents of vegetables.[Alegria,. Barberfi., Boluda, Errecalde., Farr and Lagarda 1991]. Vegetables absorb heavy metals from the soil as well as from surface deposits on the parts of vegetables exposed to polluted air[Buchaver, 1973]. Moreover, the presence of heavy metals in fertilizers contributes an additional source of metal pollution for vegetables[Yusuf, Arowolo and Bamgbose 2003].

2. MATARIAL AND METHODS

2.1. Instrumentation

The analytical determination of trace metals was carried out by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer): ELAN 9000 (Perkin Elmer Sciex Instrument, Concord, Ontario, Canada), see Table (1) highlights the operating conditions of the instruments used in this study. High purity water obtained from Millipore Milli-Q water purification system was used throughout the work.

2.2. Calibration

The ICP-MS calibration was carried out by external calibration with the blank solution and three working standard solutions (10, 20 and 30 µg/L) for all elements, starting from a 1000 mg/L single standard solutions for ICP-MS (Aristar grade , BDH laboratory supplies, England for the trace elements.

Table 1. Conditions of ELAN 9000 ICP-MS

RF power	1250 W
Nebulizer gas flow	0.92 L/min
Lens Voltage	9.25 V
Analog Stage oltage	-1762.5 V
Pulse Stage Voltage	1050 V
Number of eplicates	3
Reading / Replicates	20
Scan Mode	Peak Hopping
Dwell Time	40 mms

2.3. Sample Collection and Preparation

The soil of Tomato (Lycopersicon esculentum L.) Grown in Greenhouse Conditions and Agricultural greenhouse at Zilfi Province ,will be surved taking 10 samples of soil from the greenhouse randomly . The soils will be collected and sieved through 202 nm sieve ,and will be stored in plastic bags. (ICP-MS)spectrophotometers will be used to determine the concentrations of some Heavy Metals (Cr, Ni, Cd, Co, Hg, Zn, As, Pb, and Cu) that may be found in the soil . All samples air dried and then oven dried at 70°C for 48 h to achieve constant mass, milled and sieved. 1 g milled powder of each samples was weighed and after combusting in electrical furnace, were digested with 10 ml 2 N HCl. The resulting digest was not clear, so it was filtered through whatman filtered paper no.42.The filtered digest was transferred to a 50 ml volumetric flask and made up to mark using deionized water. A blank digest was carried out in the same way. The trace elements (Cr, Ni, Cd, Co, Hg, Zn, As, Pb, and Cu.) concentrations were determined by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) [Ataabadi, and, Najafi, 2012]. All reagents are of analytical grade and were checked for possible Heavy Metals contamination .

3. RESULT AND DISCUSSION

Concentrations of some heavy metals (Cr, Ni, Cd, Co, Hg, Zn, As, Pb, and Cu.) have been determined in the Tomato (Lycopersicon esculentum L.) agricultural soils grown in greenhouse conditions at Zilfi Province ,by using ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) . All calibration graphs are linear in the selected range of each element .The square of the correlation (r2) ranges from 0.9985-0.99999 for most of the elements in this investigation .Good precision values were obtained

Soil:

The mean concentrations of heavy metals under study for soil have been illustrated in (Table (2) and Figs.(1-9.). The most contaminated soil sample contains the maximum concentrations of three elements . This sample is found to be soil sample number (1) which contains the elements(Ni, Co, and Cu). Soil sample (4) contains the lowers concentrations of the elements (Cr, Ni, Co, Hg and Cu),so this to be the sample with lowest contamination .This may be due to excessive fertilizer ,and pesticide use ,irrigation ,atomospheric deposition and pollution by waste materials (Aydinalp and Marinova (2003).

Chromium

WHO maximum permitted level for Cr in soil is 50 mg/kg as found in the study of(Bigdeli and Seilspour 2008).So only soil sample (3) which contains 333.4 mg/kg of chromium is much polluted with this element. In this study there isn't any pollution in the other samples as they have concentrations of Cr less than permitted level of WHO. However, the presence of high clay content and intensive human activities can increase the normal contents of Cr in soils. (Micó, Peris, , Sánchez and Recatalá 2006). A specific amount of Cr (III) is needed for normal body functions, while its high concentrations along with Cr (IV) may cause toxicity, including liver and kidney problems and genotoxic carcinogen. This result agrees with Kelepertiziz (2014), which found that the maximum concentration of Cr 353.6 mg/kg. The minimum concentration of Cr is about 1.4 at sample (4), is widely different from the amount found in the previous study of (28.1 mg/kg).

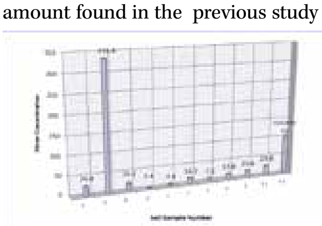

Fig.(1): Chromium Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

Nickel :

Data from table (2) and Fig.(3)showed that the soil samples are not contaminated with nickel as all the concentrations found for this element are less than maximum concentration level of WHO(50mg/kg) (Bigdeli and Seilsepour 2008). Long term exposure of Ni through the food chain may contribute to health problems like skin allergies, dermatitis, rhinitis, nasal sinusitis, lung injury and nasal mucosal injury (Rahman,. Khanam , Adyel , Islam, Ahsan and. Akbor (2012).

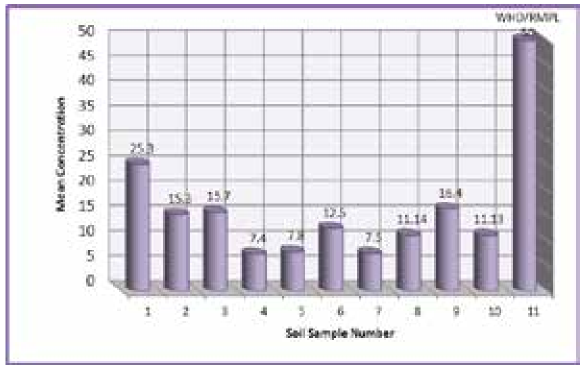

Fig.(2): Nickel Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

Cadmium

Soil sample(7) contains (8.5 g/kg) of cadmium this value was higher to WHO level for this element (3 mg/kg).So there is high contamination by Cd in this soil sample ,while other samples have no contamination by cadmium ,as the concentrations of Cd in these soil samples was less compared to WHO level . There is a growing environmental concern about Cd being one of the most eco-toxic metals, exhibiting highly adverse effects on soil health, biological activity, plant metabolism, and the health of humans and animals (Rahman et.al (2012). Cadmium affects kidney, liver, and GI tract .Concentrations of Cd in fertilizers clearly demonstrate that Cd coming from inorganic fertilizers will unlikely have an impact on Cd content in soil used in saudi Arabia (Modaihsh, Al-Swailem and Mahjoub, 2004).

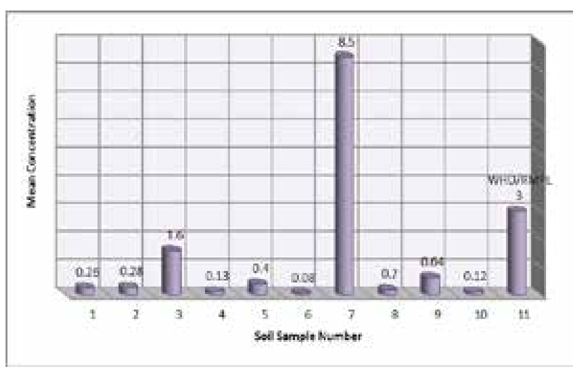

Fig.(3): Cadmium Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

Cobalt

The WHO maximum level of Co in soil is 50 mg/kg .The comparison of concentration of Co in soil samples as found in table (3.1) showed that all these values are more less than 50mg/kg. So we can say that there is no contamination of Co in soil samples, this result is in full agreement with the result obtained by (Odat and Alshammari (2011), who found that the soil samples is uncontaminated with Co.

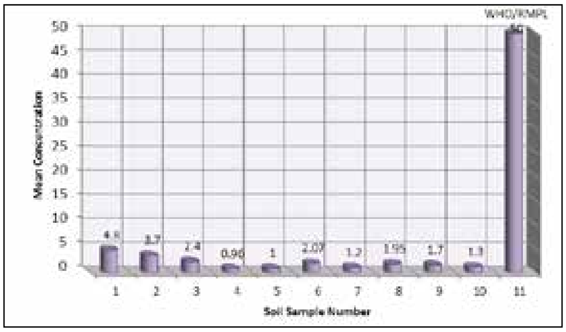

Fig.(4): Cobalt Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

Mercury

There is no pollution of Hg in soil samples ,as the higher concentration of this element (0.38mg/kg) while the maximum allowable value for this element is about 5mg/kg. Hg is a toxic metal for environmental and human health. Base-metal processing and some chemical industrial activities are the main source for Hg contamination in soils (Rahman et.al (2012).

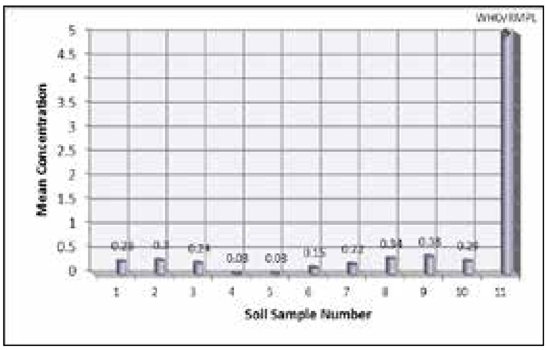

Fig.(5): Mercury Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

Zinc

The pollution limit for Zn is (300mg/kg) .The soil samples are not contaminated with Zn . The values of Zn concentrations in all samples(18.4-110.2 mg/kg) are less than the permitted value of WHO. Zinc is a very readily mobile element. High doses of Zn show toxic and carcinogenic effects and result in neurologic and hematological complications, hypertension, and kidney and liver function disorders(Rahman et.al (2012). The Zn concentrations of this study, within the range of 1.0-170 mg/reported for surface soil samples of South Carolina(Canova,1999), and different from (2.8-41mg/kg for Minna and 0.57-36mg/kg for Bida). reported by Iyaka, (2009) in their investigation of Copper and Zinc Contents in Urban Agricultural Soils of Niger State, Nigeria.

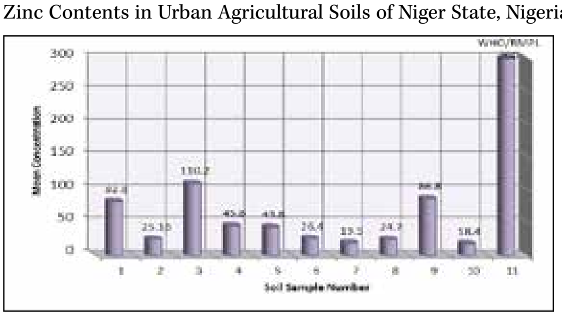

Fig.(6): Zinc Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

Arsenic

There was high pollution of As in soil samples .Five soil samples contains As concentration higher compared to WHO limit value (20mg/kg) in soil. The concentrations of As in these samples is as followes:38.8,38.7,27.5,27, and 20.8 g/kg in sample :9,10,1,2and 8 respectively. In the study of(Skála, Vácha and Čechmánková,2011) ,which evaluate arsenic occurrence in agricultural soils of the Bohemian Forest region, Arsenic concentration was found in the range from 2.1 to 183 mg/kg in the non-forest soils of the region High concentrations of As in the soils are due to significant anthropogenicity particularly industrial activities such as the metallurgical and chemical industries and the use of arsenical sprays .Arsenic is a priority toxic element that can cause arsenicosis-related disease and internal cancers, even in trace amounts(Rahman et.al (2012).

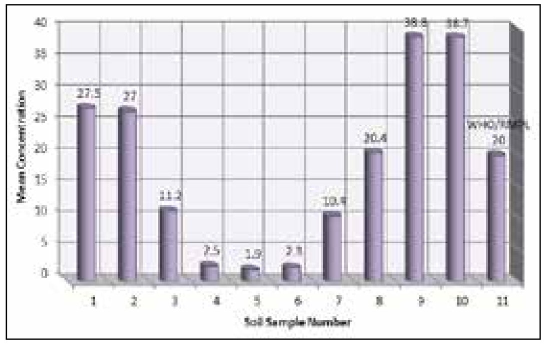

Fig.(7): Arsenic Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

Lead

The maximum Pb limit by WHO standards in soil is 100mg/kg .Data in table (2) and Fig.(8) showed that soil samples (3and 5) have the concentrations 160.2 and 154.5 mg/kg of Pb respectively .Lead concentration in these samples is more than permitted values .These values of lead indicate high pollution .Also soil sample (6) contains 88 mg/kg of Pb which indicate moderate contamination. This result was compared with the study of (Odat and Alshammari 2011) which focused on soil samples collected from two main highways, of Hail City, Saudi Arabia .The amount of Pb concentration of Odat study is about 88mg/kg in summer and 94 mg/kg in winter. Soil sample (2) have the minimum value of Pb (5.8 mg/kg), this means that this sample is of low contamination by this element .Moreover among the heavy metals, Pb is the most immobile element and its content in soil is closely associated with clay minerals, Mn-oxides, Al and Fe hydroxides, and organic material (Rahman et.al (2012), and combustion of gasoline that contains tetraethyl lead as anti –knock agent (Tuzen, 2003).

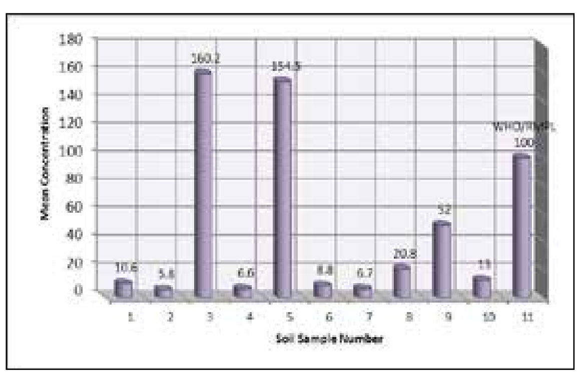

Fig.(8): Lead Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

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Copper

The copper levels (3.4-19.7 mg/kg) found in soil were within safe limits in all samples. This result agrees with (Abollino , Aceto , Malandrino , Mentasti , Sarzanini , Petrella 2002) study of heavy metal in agricultural soils from Pidmont .Italy ,which indicates total Cu concentration in range of unpolluted soil .The amount of of Cu in the study of accumulation of heavy metals in agricultural soils of Mediterranean is about 65.23(Kelepertiziz (2014).The excess use of fertilizers and pesticides will result into extensive Cu accumulation in agricultural soils .

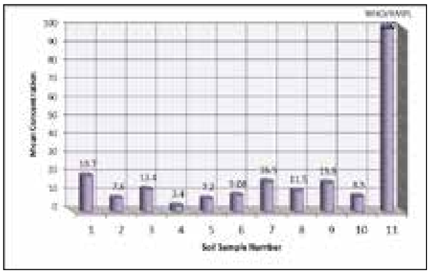

Fig.(9): Copper Mean Concentrations (mg/Kg) in 10 samples compared with World Health organization's Recommended Maximum Permissible Levels (RMPL)

4. CONCLUSIONS

The determined metal concentrations(Ni, Co, Hg, Zn, and Cu) in ten soils samples ,fit in the typical ranges of unpolluted soils ,while the elements (Cr, Cd, As and Pb) show levels concentrations more than the permitted for WHO, in some samples indicating high pollution by these elements .

Heavy metals can move from soil to plant, which poses a threat to human life. The high concentrations with Cr ,in soil may cause toxicity, including liver and kidney problems and genotoxic carcinogen. Cadmium affects kidney, liver, and GI tract . Arsenic is a priority toxic element that can cause arsenicosis-related disease and internal cancers, even in trace amounts. A further study can be made of the causes of increased concentrations of these elements.

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Element	Soil number									
	1	2	3	4	5	6	7	8	9	10
Cr	24.4±0.2	333.4±2.7	20.2±0.16	1.4±0.07	4.8±0.03	13.7±0.1	7.5±0.09	13.8±0.262	15.8±0.095	24.8±0.64
Ni	25.3±0.5	15.3±0.2	15.7±0.3	7.4±0.08	7.8±0.09	12.5±0.1	7.5±0.008	11.14±0.412	16.4±0.295	11.13±0.21
Cd	0.26±0.01	0.28±0.002	1.6±0.05	0.13±0.005	0.4±0.004	0.08±0.0007	8.5±0.102	0.2±0.003	0.64±0.015	0.12±0.002
Co	4.8±0.07	3.7±0.037	2.4±0.022	0.96±0.027	1.0±0.008	2.07±0.024	1.2±0.006	1.95±0.059	1.7±0.022	1.3±0.042
Hg	0.28±0.001	0.3±0.007	0.24±0.001	0.03±0.001	0.03±0.001	0.15±0.002	0.22±0.002	0.34±0.010	0.38±0.008	0.29±0.012
Zn	82.8±1.4	25.16±0.35	110.2±1.32	45.8±0.78	43.8±0.31	26.4±0.1	19.5±0.098	24.7±0.667	86.8±1.3	18.4±0.66
As	27.5±0.6	27.0±0.2	11.2±0.3	2.5±0.10	1.9±0.046	2.3±0.04	10.4±0.177	20.4±0.308	38.8±0.854	38.7±0.58
Pb	10.6±0.25	5.8±0.16	160.2±3.1	6.6±0.18	154.5±1.39	8.8±0.08	6.7±0.174	20.8±0.374	52±2.18	13±0.52
Cu	19.7±0.4	7.6±0.13	12.4±0.11	3.4±0.05	7.2±0.022	9.08±0.1	16.5±0.066	11.5±0.38	15.9±0.16	8.5±0.27

Table 2. Elements Mean Concentrations in Soil Samples

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