

Concentration of Cadmium, Lead and Chrome in Some Vegetables Amended with Phosphate and Urea Fertilizers for More Than Forty Years

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Received: 24 May 2018

Published: 07 June 2018

Keywords: *Heavy Metals; Soil; Vegetables; Contamination; Fertilize; Correlation*

Abstract

Ashati agriculture project built in 1975 for the production of vegetables and grasses for animals. Since that time vegetables were grown and fertilized by phosphate and urea chemical fertilizers. therefore this investigation was conducted to study the state of the accumulation of some heavy metals such as Cd, Pb and Cr. in some selected vegetables which include *Solanum tuberosum* (Potatoes), *Allium cepa* L. (Onion), *Daucus Corota* L. (Carrot), *Cucurbita Pepo* (Courgette), *Solanum melongena* L. (Eggplant), *Lactuca sativa* L. (Lettuce), *Petroselinum crispum* (mill.) Nym. (Parsley) and *Spinacea oleracea* (Spinach). The mean levels of these heavy metals were ranged from 0.0-0.03, 0.0-2.36 and 0.0.0-8.13ppm for Pb, Cd and Cr. respectively. Soil samples were also collected from the same sites of collected vegetables, concentration of these metals in the soil were 0.38, 0.87 and 1.75ppm respectively.

Among the vegetables studied Cd and Cr exceeded the allowable limits in some vegetables whereas concentration of Pb is under the detectable limit. The results also shows phosphate fertilizer contains 1.15 and 3.3ppm of Cd and Cr respectively, while Urea contains 0.14ppm of Cr as impurities. Concentration factor of Cd (1.21 - 7.38) and Cr (1.22 - 6.84) had exceeded 1.0 which indicate that concentration of these elements are much higher in vegetables samples than in soil. Statistical analysis shows there is a positive correlation between Cd and Cr at 0.01, and also between Cd and Cr, Cd and Pb at 0.05 level, positive correlation at 0.01 level were also observed between cultivated and uncultivated soil, urea and cultivated and uncultivated, while these is negative correlation between phosphate fertilizer and cultivated soil, phosphate and urea.

Introduction

Vegetables are very important for the human being as they constitute major component of his diet. it's a major source of minerals, trace elements, vitamins, carbohydrates and proteins. its consumptions is increasing gradually in recent years particularly among the urban communities [1]. Cultivation of these vegetables in a contaminated soils can lead to the accumulation of heavy metals in their edible and non-edible parts [2]. Cultivated soils can be polluted with heavy metals due to irrigation with polluted water, addition of fertilizers, pesticides or industrial emissions [3]. Vegetables become contaminated either due to soil pollution or due to long exposure to polluted environment [4]. Plants absorb small amounts of contaminants heavy metals compounds together with an essential elements and can translocate them through their various organs and tissues to the food chain [5,6]. High concentration of Heavy metals in soil are toxic to most plants, they can compete with essential mineral nutrients for uptake thereby disturbing the mineral nutrition of plants or after uptake by plants they accumulate in plants tissue and cell components and hampers the general metabolism of the plant [7-10].

It has been reported that heavy metals has multiple direct and indirect effects on plant growth and alerts several physiological functions by forming of complexes with N, O and S ligands [11]. High concentration of heavy metals can interfere with mineral uptake, protein metabolism, water relations, membrane functioning and germination [12-15]. Soils contaminated with heavy metals leads to lower the leaf production rate and the plant mass as well as poor development of flowers [16]. Vegetables can take up heavy metals either by absorbing them from contaminated soils or from deposits on different parts of vegetables exposed to the air from polluted environments [17]. The uptake of heavy metals by roots mainly depends on metal and soil characteristics and plant species, however metal mobility in plants is very important to determine the effect of soil contamination on plant-metal uptake [18,19], it is also depends on other different factors such as their soluble content in it, types of plant species, fertilizers and soil, plant growth stages and soil pH [20,21]. It has been reported that plant species have a variety of capacities in removing and accumulating heavy metals [22], however it has been indicated that some species may accumulate specific heavy metals. Uptake of heavy metals by vegetables are effected by concentration of heavy metals in soil, climate, atmospheric deposition, nature of soil on which vegetables grown and the degree of its maturity at time of harvest [23].

Contaminated soil determine the metal distribution in different parts of the plant by metal translocation process in plant species, accumulation of metals from soil to plant parts didn't follow any particular pattern but varied with respect to metals, plant species and its produce [24]. The rate at which heavy metals are accumulated in the soil depends on different factors such as soil's physicochemical properties and the relative efficiency of the crops to remove the metals from the soil [25]. Potentially harmful heavy metals contents in soils may not come only from bedrock itself but also from other source like solid or agriculture inputs, liquid waste deposits and fallout of industrial emissions [26].

Some heavy metals such as Co, Mn, Ni, Zn, Cu, Fe and Cr are considered as an essential component metals at low concentrations for biological activities in human beings and plants, whereas its present in elevated levels can cause problems to them. While other non-essential heavy metals such as Cd, Pb, As and Hg are play a toxic role to living organisms [27].

Vegetables take up heavy metals from contaminated soils through the crop root and incorporated them into the edible parts of plants tissues or as a deposits on their surfaces from the air [28,29]. It has been reported that leafy vegetables accumulated Heavy metals in their edible parts easily compared to grain or fruit crops [30]. Heavy metals are harmful because of their non-biodegradable nature and their potential to accumulate in different body parts [31]. Prolonged consumption of high concentrations of heavy metals through foodstuffs leads to a number of nervous, renal, cardiovascular, neurological impairment as well as bone diseases and several other health disorders [32-34]. Foodstuffs polluted with Heavy metals can severely minimize some vital nutrients in the body that are accountable for declining immunological defenses, reduced psychosocial abilities, growth delay, incapacities related with malnutrition and greater occurrence of upper gastrointestinal cancer degrees [31,35-36].

The main objective of this investigation is to evaluate the concentration of some heavy metals Cd, Pb and Cr as a result of long term, cultivation and fertilization. in some cultivated vegetables and soil in Ashati agriculture project.

Materials and Methods

Sampling Site

This study was carried out on Ashati agricultural project at Fezzan province situated in Southern - West corner of Libya between North latitudes 23° to 28.5° and East longitudes 10° to 16°, with an altitude of 400m above sea level [37]. This project built in 1975, It contains 24 wells each well contains 12 farms. Soil texture of the experimental area is mostly sand loamy soil, fertile and have very good drainage system. It is one of the major sources for the vegetables production in the area. Two farms were selected to determine the heavy metals concentration in vegetables, fruits and soils samples.

Collection of Vegetables and Soil Samples

Vegetable samples were collected during (Dec, Apr, Jul. and Oct. 2013 -2014) which represent different seasons of cultivation. The vegetables collected which represent leafy, roots and fruits were, *Petroselinum crispum* (Parsley), *Spinacia Olerac* (Spinach), *Lactuca sativa* (Lettuce) *Solanum tuberosum* (Potatoes), *Allium cepa* (Onion), *Daucus Carota* (Carrot) *Solanum Melongena* (Eggplant), and *Cucurbita Pepo* (Courgette) Vegetables samples were brought to laboratory edible parts wash thoroughly with clean tap water and then by distilled water to remove the suspended particles. Samples were dried in oven for 24 hours at 65-70°C. grind to a fine powder in a manual grinder and kept in clean, dry stopper plastic containers at room temperature. Soil samples were also collected from the same place, about 1.0kg of soil samples from depths of (0-30cm), samples were taken by soil Auger in a clean polyethylene bag, air-dried for two weeks, large clods were crushed to facilitate the drying. The dried soil samples were crushed in a porcelain mortar with pistol and sieved through 2mm sieve.

Extraction of Heavy Metals

In Vegetables Samples

The procedure used for the extraction is based on the procedure described by [38]. 1.0 gram of dry powder vegetable taken in a digestion flask, 5.0ml of HNO_3 added and heated till the brownish fumes were disappeared 5.0ml HClO_4 , and 10.0ml of HCl were added, the mixture heated till the mixture became transparent. The resulting solution was cooled and filtered with whatman No. 42 filter paper. Finally the extract of the digestion was transferred to a 50ml volumetric flask and made to volume with ultrapure water.

In Soil Samples

For extraction of heavy metals from soil samples, 1.0g of sieved soil were taken in a crucible, 1.0ml of concentrated HNO_3 added and heated till the acid totally evaporated, after cooled in a room temperature the crucible placed in a muffle furnace at 600°C for 6 hours, after cooled at room temperature, the ash washed three times about 10ml each with diluted of 1.5% NH_3 and filtered by whatman 42 filter paper in a 50ml volumetric flask the volume made up to the mark with double distilled water. heavy metals were also determined in the chemical fertilizers (di-ammonium phosphate DAP and urea (46%) which used for fertilization.

Measurement of HMs were made by atomic absorption spectrophotometer (NOVA A400). Calibration curves were prepared for each element individually applying linear correlation by least square method. a blank reading was also taken and necessary correction was made during the calculation of concentration of various elements.

Results and Discussion

Heavy Metals in Soils (Cultivated and Uncultivated) and Chemical Fertilizers

The concentration of heavy metals in cultivated, uncultivated, phosphate and urea fertilizers used for fertilization are presented in Table-1. The concentration of Pb, Cd and Cr in rhizosphere soils collected from the farms are 0.0, 0.4 and 0.86ppm respectively. However concentration of Cr in this soil samples were less than that of uncultivated soil which used as reference. The existence of (Cr) higher than that in cultivated soils might be referees to the composition of uncultivated soils. In general concentration of heavy metals in the examined soil doesn't exceed the limited values for agricultural soils which recommended by [39]. These results are compatible with the results obtained by [40].

Analysis of phosphate fertilizers (DAP) and urea table-1. Indicated that high concentrations of Cd 1.15ppm and Cr 3.3ppm were reported in DAP, while Pb where not exist. Permissible limits of these elements are 0.3, 2.3 respectively [39]. Phosphate fertilizers have been reported contain high amounts of HM including Cd and Ni [41]. However HM in urea fertilizers were within the permissible limit [39]. Table-1 Shows that there is strongly relationship between the concentration of the element in the soil solution and/or type of fertilizer and its concentration in the vegetable samples. It had been reported that accumulation of HMs from soils to plants depends on many factors such as metal forms, soil properties and plant species and parts [42].

Table 1: Concentration of Heavy metals in samples of soil, fertilizers and irrigation water (ppm)

Sample HM (ppm)	Cultivated Soil	Uncultivated Soil	Phosphate (DAP)	Urea
Pb	-	-	-	-
Cd	0.4	-	1.15	-
Cr	0.86	27.83	3.3	0.14

(-) = Not Detected

Heavy Metals in Vegetables Samples

Vegetables either leafy (Lettuce, spinach and parsley), roots (Carrot, Onion and potatoes) or fruits such as (Courgette and eggplant), were shows variations of it is content in their accumulation of heavy metals. Table -2. shows that leafy vegetables such as Parsley, Spinach and Lettuce were accumulated more HMs compared to grain or fruit crops. This findings are agree with the results reported [30]. Heavy metals concentrations obviously indicated variations among different vegetables collected as appeared in table -2. It had been reported that variations in heavy metal concentrations in vegetables grown in the same site attributed to the differences in their morphology and physiology of the heavy metal uptake, exclusion, accumulation and retention [43, 44], it is also reported that the uptake of metal ions influenced by the metal species and plant parts [45, 46].

Uptake of high levels of heavy metals by leafy vegetables may be due to higher transpiration rate to maintain the growth and moisture content of these plants [47]. The trend of heavy metals concentration in vegetables is = Cr>Cd>Pb

Table 2: Concentration of heavy metals in vegetables samples (ppm)

Sample \ HM (ppm)	Pb	Cd	Cr
Courgette	-	1.39	0.88
Egg plant	-	-	-
Potatoes	0.014	0.85	1.37
Onion	-	2.36	6.16
Carrot	-	1.69	2.46
Lettuce	0.03	1.14	1.56
Spinach	-	1.05	2.13
Parsley	-	2.36	8.13

(-) = Not Detected

Cadmium was detected in all samples except Eggplant, the results shows that high concentration of Cd reported in Onion and Parsley (2.36)ppm in both of them. it is concentration in Potatoes, Spinach, Lettuce, Courgette and Carrot were 0.85, 1.05, 1.14, 1.39 and,1.69ppm respectively. Variation of the concentration of Cd to different vegetables may be due to differential capacity of the examined vegetables. We attribute the accumulation of Cd in vegetables to the application of huge amounts of phosphate fertilizers by farmers. Phosphate fertilizers are the major source of Cd as it is naturally found as an impurity in phosphate rocks [45], it had been reported that soils accumulate Cd as a results of the application of huge amounts of phosphate fertilizers [48]. Cadmium is a highly mobile metal it can easily absorbed by the plants through root surface and moves to wood tissue and then transfer to upper parts of plants [49]. High concentration of Cd reported in lettuce and spinach grown in urban areas and in Spinach and Coriander and also in Parsley, Onion and Lettuce [50-53].

Lead content in the vegetables of the present study sites were within the permissible limits [39], its concentration in vegetables is generally very low due to its low bioavailability. Pb concentrations in most of vegetables samples studied was under the detection limit of the instrument, however concentration of 0.014 and 0.03ppm recorded in Potatoes and Lettuce respectively. although its recorded in the soil samples 6.45ppm in table-2, Pb is known to be toxic and harmful to plants, despite many plants usually show some ability to accumulate high concentrations of lead without visible changes in their appearance or yield. Contamination of vegetables by heavy metals may occur due to irrigation with contaminated water, emissions from industries, addition of fertilizers and metal based pesticides [54].

High concentration of Pb has been reported in many vegetables and fruits grown in vicinity of industrial areas, irrigated with sewage or treated wastewater [52,55]. High concentration of Pb were reported in vegetables irrigated with polluted water in Hamadan city Iran [56]. We attribute the low concentration of Pb in the vegetables samples to the locate of the study area away from industrial complexes, traffic roads and it's irrigation with underground water, high concentration of Pb (17.54-25.00ppm) were reported in vegetables grown in industrial areas [21]. Our results were in agreement with the results reported by [57].

The Chromium content in selected vegetables exceeded the maximum permissible value of 0.05ppm determined by [39]. except Eggplant. The significant high concentration of Cr was recorded in Parsley and Onion with 8.13 and 6.16ppm this results is compatible with the findings by [58]. Other examined vegetable were had different values of Cr table-1. The ability of different crops in accumulating heavy metals influences their concentrations in the edible parts [59]. In a survey conducted by [60] to determine the concentration of some metals in a leafy vegetables collected from the markets, the concentration of Cr was under the detection limit of the instrument. Whereas high concentration of Cr (6.9 -7.4ppm) close to our results were observed in vegetables in the vicinity of industrial area of roadside [61]. As the samples were collected from farms fertilized with a chemical fertilizers for long time and the analysis of the soil showed high concentration of Cr table-2, we believe that the source of Cr in the vegetables was probably the agriculture lands which fertilized by inorganic fertilizers and synthetic pesticides for a long period [58].

Concentration Factor of Heavy Metals in the Vegetables

Concentration factor of HM were also calculated as the concentration of HM in vegetables sample relative to the concentration of HM in soil (Table-3). According to the equation below (1).

$$\text{Concentration Factor}(CF) = \frac{\text{Concentration of HM in vegetable sample}}{\text{Concentration of HM in soil}}$$

The (CF) is ranged from 0.002 - 7.38 highest CF were observed in Onion with Cd. However bigger value of CF means that Conc. Of HM in vegetables are more than conc. of these metals in soil. We might explain this as the vegetable samples were accumulating the HM while in soil its leached down by water, as the soil texture is sandy. The results shows that CF of Cd is high in all samples. Low CF were observed with Pb (0.002 - 0.004) this result is consistent with the results reported by [2,62] reported that, metal ions in soluble forms are readily uptake by Plants, exchangeable forms of elements in soil have the highest solubility and metals associated with carbonate are also easily soluble.

Table 3: Concentration factor for Trace Metals in the Vegetables

Vegetable Metal (ppm)	Cour- gette	Eggplant	Potatoes	Onion	Carrot	Lettuce	Spinach	Parsley
Pb	-	-	0.002	-	-	0.004	-	-
Cd	4.34	-	2.66	7.38	5.28	3.56	1.21	2.71
Cr	0.98	-	1.52	6.84	2.73	1.73	1.22	4.65

Statistically significant correlation coefficients at 0.01 and 0.05 probability level were measured between metal concentrations, the results shows good correlations at 0.01 between Cr and Cd. While at 0.05 there is good correlations between Cr and Cd, and Cd and Pb. these results were compatible with the results reported [63].

Table 4: Acute toxicity study of *Annona senegalensis* stem bark methanol extract

	Cr	Cd	Pb
Cr	1		
Cd	0.993**	1	
Pb	0.923*	0.894*	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Correlation of heavy metals concentration in cultivated soil, uncultivated soil, phosphate (DAP) fertilizer and urea (table -5) shows that there is high significant correlation at P= 0.01 level between cultivated and uncultivated soils; uncultivated soil and urea. Phosphate fertilizer doesn't shows any correlation with any of measured parameters whereas urea shows high correlation with cultivated soil, uncultivated soil but not with phosphate fertilizer.

Table 5: Correlation of heavy metals in cultivated, uncultivated soils. Irrigation water, phosphate fertilizer (DAP) and Urea.

	Cultivated Soil	Uncultivated Soil	Phosphate Fertilizer (DAP)	Urea
Cultivated soil	1			
Uncultivated soil	0.998**	1		
Phosphate fertile. DAP	0.007	0.009	1	
Urea	0.991**	0.989**	0.103	1

** . Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Conclusions and Recommendations

As mentioned above Ashati agriculture project built more than 40 years ago to provide the area population with vegetables and fruits, because of the low fertile of the soil in the area due it's sandy nature and low organic matter therefore chemical fertilizers (phosphate and urea) and manure were used for fertilization. Farmers added a lot of chemicals to increase their vegetables production. This study indicated that long-term and indiscriminate application of chemical fertilizers and organic manure lead to the accumulation of some toxic heavy metals Such as Cd and Cr while the Pb was within the permissible limits designated by FAO/WHO. Concentration of heavy metals were varied among the vegetables (leafy, fruits or roots) tested, the variation of heavy metal accumulation reflects capabilities of vegetables to uptake and translocate of HM in their edible parts.

This study is the first to analyze some heavy metals in some vegetables grown and consumed in Ashati and vicinity area. Concentrations of heavy metals must be monitoring regularly to make sure it's concentrations are within the permissible limits. Chemical fertilizers must be also added wisely to avoid any contamination from them.

Acknowledgement

The authors gratefully acknowledge the central laboratory of Sebha university for their support to do the elemental analysis.

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