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PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSInet

Asian Network for Scientific Information

308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Pakistan Journal of Biological Sciences 5(4): 471-473, 2002

Bioavailability of Chromium in Vegetables of Selected Agricultural Areas of Malaysia

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Abstract: A study was conducted in 2 agricultural areas (Sepang and Bangi) to determine bioavailability of chromium in soil and the potential uptake of chromium in selected vegetables. A total of 6 vegetables namely *Brassica nigra, Ipomea aquatica, Capsicum annum, Vigna sinensis, Manihot esculenta and Ipomea batatas* were selected for chromium analyses in leaves, fruits and roots. Chromium content in vegetables of fruity and root type was higher compared with the leafy vegetables. Concentration of chromium in soil was low at both study areas.

Key words: Bioavailability, chromium, sequential extraction, soil, vegetables

Introduction

Heavy metals occur naturally in rocks, soils and water but their anthropogenic components have increased since the Industrial Revolution. This has caused serious problems concerning food chain and consequently, the health of organisms, including human being (Otero *et al.*, 2000a). Heavy metals content in a soil depends on the nature of its parent material. As soil matures, leaching and nutrient cycling through plants will cause some elements to be concentrated in specific soil horizons while others will lost progressively in drainage water (Wild, 1988).

Chromium is one of the heavy metals that have nutritional importance (Kabata-Pendias and Pendias, 2001). Due to industrial activities, large quantities of Cr compounds are discharged in liquid, solid and gaseous wastes into environment and ultimately have significant adverse biological and ecological effects (Kotas and Stasicka, 2000). The main source of Cr in natural soils is weathering of their parent materials. The average amount of this element in worldwide soil surface is 54 ppm according to Kabata-Pendias and Pendias, 2001).

The two common oxidation states of Cr present in the environment, are Cr^{3+} and Cr^{6+}. The first one is considered to be the trace element essential for proper functioning of living organisms. While Cr^{6+} was reported to exert toxic effects on biological systems and is known as the most mobile Cr form in soil and water systems, whereas Cr^{3+} is generally not transported over great distances because of its low solubility and tendency to be adsorbed in the pH range typical for natural soils and waters. Hexavalent anionic form is more available for living organisms than is Cr^{3+}, and plays a main role in removing this metal from water and soil systems (Kotas and Stasicka, 2000).

Plants grown in heavy metal contaminated soil often show metal accumulation, particularly in root tissue and the rate of Cr uptake is dependent on several soil and plant factors (Kabata-Pendias and Pendias, 2001). The mechanism involved in the uptake and translocation of chromium in plants is not understood, because of uncertainty about the ionic species present in different systems. There is, however, evidence that Cr^{6+} is reduced to Cr^{3+} between the root surface and shoots and that irrespective of the form in which it is supplied most of the chromium is retained in roots (Wild, 1988).

Vegetative roots absorb nutrient elements from soil that are then returned to surface through leaf fall. The uptake of heavy metals by vegetable depends on the mobility and availability of metals in the soil. Factors that affect the mobility of heavy metals including: 1) chemical parameters such as pH, Eh (redox potential), organic matter content, salinity, concentrations of competing ions, ionic or anionic complexes, moisture, 2) physical parameters such as texture (size distribution) plus structure and penetratability, presence of one or an assemblage of clay minerals, their surface areas and cation exchange capacities, presence of oxyhydroxides of Fe, Mn and Al and carbonate minerals, climate (temperature) and 3) biological parameters such as microbial activity, vegetative root extension and penetration, and burrowing organisms (Siegel, 1998). The purpose of this study was to determine the bioavailability of Cr in the soil and the potential uptake of Cr by vegetables.

Materials and Methods

Six types of vegetables comprising leaves, fruits and roots have been studied from Sepang and Bangi, Selangor. Both soil areas were sandy and peat soil respectively. Vegetables studied were *Brassica nigra* and *Ipomea aquatica* for leaves, chili (*Capsicum annum*) and long bean (*Vigna sinensis*) for fruits, tapioca (*Manihot esculenta)* and ubi keledek (*Ipomea batatas)* for roots. Sampling was done randomly at three different times of sampling.

After harvesting vegetables were brought to the laboratory and washed with pipe water to remove the soil followed by three times with distilled water. Samples were cut into small pieces with plastic knife before oven drying at 70°C until the weight became stable. Samples then were ground with mortar and weighed followed by wet digestion in the conical flask with HNO_3: $HClO_4$ (2:1) for 2-3 hrs on sand bath (AOAC, 1984). Ten ml of HCl was added to solute inorganic and oxides salt. Digested samples were filtered with 0.45 µm pore size Milipore filter paper made up to 100 ml with distilled water. Heavy metals concentrations were determined by atomic absorption spectrometry (AAS) by Perkin Elmer model 1100B.

Soils were collected at 0-30 cm depth randomly from sampling areas and air dried at room temperature in the laboratory. After that the soils were ground with mortar and sieved to pass through 250 µm. Heavy metals from easily leachable and ion exchange were extracted using 1.0M NH_4CH_3OO (pH 7). Ten grams of soil samples were added with 50 ml solute (Badri, 1984). Samples then were stirred for 1 ½ hrs and centrifuged for ½ hrs at 3000 rpm before filtered through 0.45µm pore size filter paper and brought to 50 ml volume with distilled water. Adding 50 ml distilled water and followed by shaking and centrifuged in the same way washed samples. Concentration of metal in soil samples was determined by atomic AAS (Perkin Elmer model 1100B). All analyses were conducted in three replications. Carbon organic analysis was determined.

Results and Discussion

Concentration of Cr in vegetables is shown in Fig. 1. The Cr content in fruity vegetables (*Vigna sinesis* and *Capsicum annum*) and root type vegetables (*Ipomea batatas* and *Manihot esculenta*) were higher when compared to the leafy vegetables. Chromium content in both leafy vegetables (*Brassica nigra* and *Ipomea aquatica*) were very low and not detectable at two agricultural areas. This somewhat differs from the findings of Kumar *et al.* (1995), who discovered that *Brassica* sp. for example the Indian mustard have an unusual ability to take up heavy metals such as Pb, Cr, Cd, Ni, Zn and Cu from roots substance and concentrate these metals in their tissues. Kabata-Pendias and Pendias (2001) observed that higher Cr content was detected in roots than in leaves and shoots and the lowest can be seen in grain.

Zayed *et al.* (1998) indicated that all plant tissues tested (root or shoot) of several vegetables crop only showed the accumulation of Cr^{3+} . These results suggested that plant tissue are able to convert the potentially toxic Cr $_4^{-2}$ (Cr^{6+}) into non-toxic Cr^{3+} species. This conversion occurred in root tissue and Cr^{3+} was detected to bind to cell walls of roots and thus limit the translocation of Cr^{3+} to shoot.

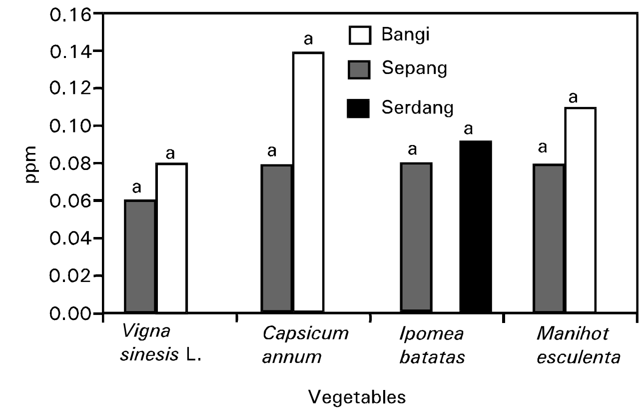

Fig. 1: Average chromium content in selected vegetables

Our findings also showed that the level of chromium detected in other fruity and root type vegetables was lower in Sepang as compared to Bangi. However the difference was nonsignificant. This is not surprising as soil in Sepang was found to be more acidic with higher percentage of particle size and organic carbon (Table 1). The content of Cr in various parts of vegetables studied were between 0.02 to 0.14 ppm and this seemed to agree with the findings of Kabata-Pendias and Pendias (2001), that Cr content

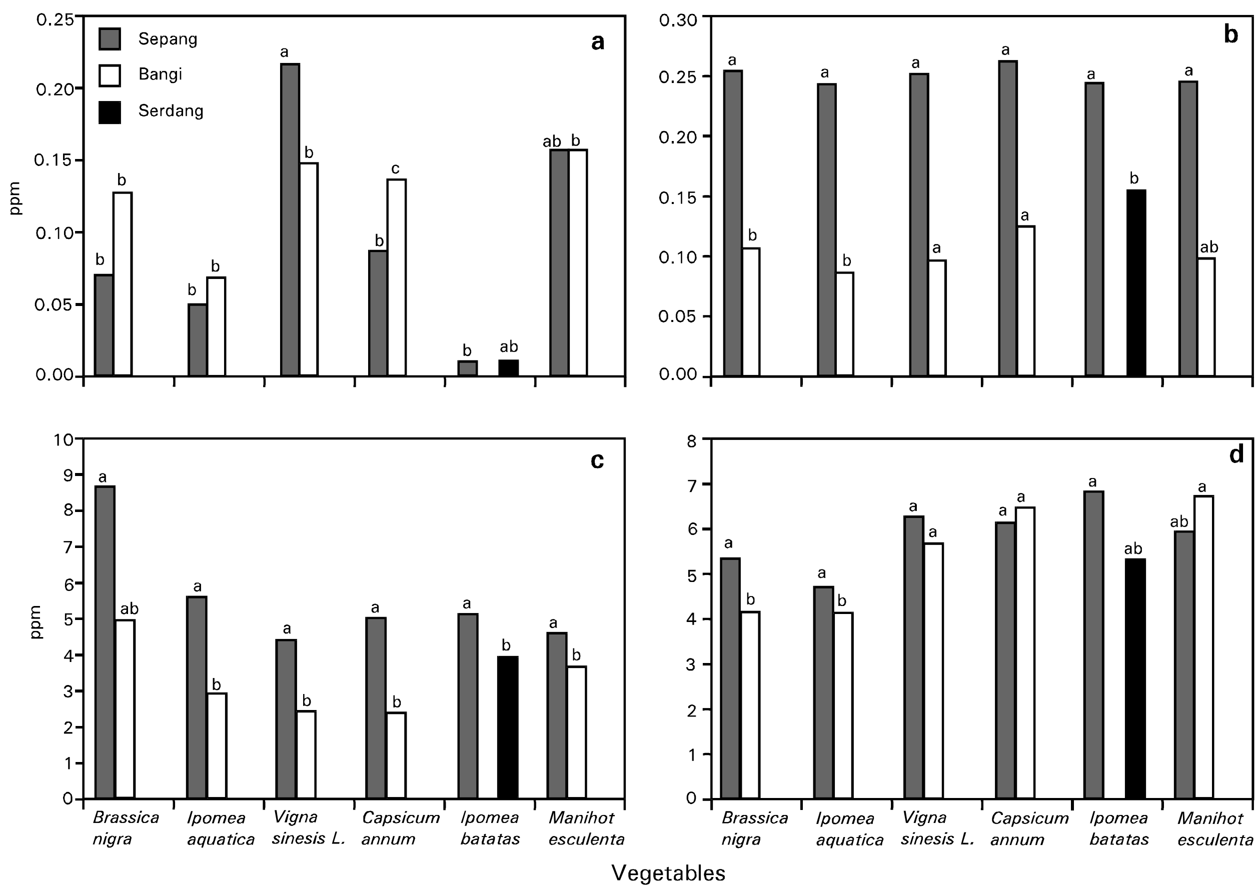

Fig. 2: a) Average chromium levels in soil (acid reduction). b) Average chromium levels in soil (easily and freely leachable fraction) c) Average chromium levels in soil (organic oxidation) d) Average chromium levels in soil (resistant fraction)

Table 1 : Physical properties of soil samples

Area	Soil pH	% particle size	% organic carbon
Bangi	6.88	11.6	1.16
	6.77	10.0	1.00
	6.67	-	1.40
	6.85	13.55	1.29
	6.77	22.38	1.27
Mean values	6.78	14.38	1.22
Sepang	3.66	28.33	35.90
	4.29	20.74	29.35
	4.40	49.67	27.39
	4.56	54.97	27.05
Mean values	4.23	38.42	29.92
Serdang	4.17	31.28	1.30
Mean values	4.17	31.28	1.30

in plant material were usually in the order of 0.02 to 0.20 ppm (Kabata-Pendias and Pendias, 2001). In most studies it has been found that the levels of chromium in plants are less than 1 to 2 µg/g dry matter even when growth is reduced to toxicity, but certain species which have become adapted to soils developed on ultra basic rocks accumulate and are tolerant to both chromium and nickel (Wild, 1988).

According to Kabata-Pendias and Pendias (2001) most soils contain significant amount of Cr, but its availability to plants is highly limited. The addition of Cr to soil affects Cr content of plants, and the rate of Cr uptake by plants is dependent on several soil factors. The bioavailability and toxicity of heavy metals depend on the forms in which these elements are found associated with different components of soils and sediments (Otero *et al.*, 2000b).

The Cr content in the soil was slightly higher in resistant and organic oxidation followed by easily leachable and ion exchange and acid resistant fractions (Fig. 2a-d). Overall the concentration of Cr in the soil from studied area was low. The easily leachable and ion exchange fraction represents metals that exist in loosely held bond or absorbed on exchangeable surfaces of clay minerals and organic matter and thus available to be absorbed by plants (Badri, 1984). In the easily leachable and ion exchangeable fraction (EFLE) of soil taken from each vegetable sampling areas, higher concentration of chromium (0.2-0.27 ppm) was detected in Sepang (Fig. 2b). When compared to soil in Bangi and Serdang, all chromium concentration in EFLE in Sepang was found to be significantly higher ($p < 0.05$) except for soil around sampling area for *Ipomea batatas.*

In the acid reducible fraction (AS) (Fig. 2a) significantly ($p < 0.05$) higher concentration of chromium was detected only in soil around *Vigna sinesis* sampling area. However soil around the leafy vegetables and *Capsicum annum* were found to be lower in Bangi area with significant difference ($p < 0.05$) for the soil around *Capsicum annum.* The soil around root vegetables were found to be equivalent in amount in both agricultural areas.

Chromium concentration in organic compound fraction (OO) were higher in Sepang soil sample for all vegetables. All soil samples in both Sepang and Bangi showed significant difference ($p < 0.05$) in terms of chromium concentration with the exception of soil samples taken from *Brassica nigra* sampling area (Fig. 2c). In the last soil fraction namely the resistant fraction (RR), the chromium concentration in Sepang soil were higher in all vegetable sampling areas except soil for *Capsicum annum* and *Manihot esculenta.* However significant difference ($p < 0.05$) was only found between soil samples of leafy vegetables in Bangi and Sepang.

The concentration of Cr found in all fractions from this study was very low compare to other places. The average amount of this element in various kinds of soils ranges from 0.02 to 58 µmol/g (Coleman, 1988; Richard and Bourg, 1991). They also discovered that the increase in local Cr concentration in soils originates from fallout and washout of atmospheric Cr-containing particles as well as from chrome-bearing sludge and refuse from industrial activity.

Siegel (1998) reported that the elements Cr in the soil is tightly bound in the residual phase and nor easily mobilized whereas other elements like Cd has more distribution in easily soluble and exchangeable phase the other elements considered.

Previous study by He and Singh (1993) indicated that Cr concentration increased with increasing values of soil cation exchange but decreased with increasing soil pH. In this study the correlation was found only between Cr in the *Manihot esculentus* ($r = 0.96$) (0.01) and metals extracted from easily leachable and ion exchange fraction and between Cr ($r = 0.95$) ($p = 0.01$) and soil pH from Bangi. Research done by He and Singh (1993) showed a significant correlation between Cr ($r = 0.35$) ($p = 0.05$) in the easily leachable and ion exchange fraction and in the soil studied. Chromium content in vegetables and soils studied were generally higher than other studies stated in the literature for similar research. These results suggested that the degree of Cr pollution in the study areas was quite low compare to other places and thus indicating that the bioavailability of Cr to vegetables was also minimum.

In conclusion the Cr content was found higher in fruit and roots than leaf vegetables. The level of Cr was generally lower in the vegetables studied and still below the Malaysian Food Act 1984 (MOHM., 1999). The Cr content in the soil also was generally low compared to other types of soil and bioavailability of Cr in this study was found not related to the Cr content in soil.

Acknowledgment

The authors are very thankful to University Kebangsaan Malaysia for providing research funding ST/8/2001 to conduct this research.

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