Investigation of Trace Metals in Vegetables Grown with Industrial Effluents

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(Received 11th June, 2002, revised 13th May, 2005)

Summary: Fruits and vegetables are the major sources of minerals vitamins, carbohydrate, protein and fiber. Controlled conditions must be provided during harvesting of vegetable and fruit. The reason behind this study was an observation, that untreated industrial water was used for the harvesting of vegetables near Korangi Industrial Area (KIA). Spinach, sponge gourd and tomatoes samples were investigated for heavy metals such as Cd, Co, Cr, Cu, Fe, Pb, Hg, Mn, Ni and Zn. Pb was found to be maximum among all metals investigated in vegetable and tomato samples as 242.5, 46.3, 64.8 mg/kg for spinach, sponge gourd and tomatoes respectively. Hg was found to be minimum amount among all metals investigated as 0.18, 0.95 and 0.05 mg/kg for spinach, sponge gourd and tomatoes respectively. A distinct variation in concentrations of all other metals was observed for the three vegetables. Metal accumulation in soil and vegetables was also studied, which was found to be maximum for Pb and minimum for Hg.

Introduction

Karachi is the biggest industrialized city of Pakistan; Population of Karachi is estimated as 10 million [1]. It is the center of professional and commercial activities and only port city of Pakistan. As the large industrial city of Pakistan it has two planned industrial area viz. Korangi Industrial Area (KIA) and Sindh Industrial Trading Estate (SITE). SITE covers an area of about 16 km^2 containing approximately 500 major industries, 60% of which are textile mills and other are diverse types dealing with chemicals, detergents, iron and steel, vegetable oils, beverages and food products [2]. KIA is located in district Malir, has a total area of 34.4 km^2, having 2000 various types of small and medium sized industries [3]. However, leather industry and textile industries are dominating industries of KIA [4].

The investigation of environmental pollution has gained a lot of attention now a day. Different substances occur naturally in our environment as a consequence of natural events. Many diseases are caused by the inability of environment to support the mineral needs of human, plants and animals in adequate, safe or non-toxic amount [5]. Heavy metals have great significance due to their tendency to accumulate in the vital human organs over prolonged period of time. Plants are more sensitive to pollutants than animals or man [6]. Untreated sewage and industrial water is commonly used for the cultivation of vegetable around the urban area of Pakistan. Different studies have been carried out to estimate the heavy metal contents in vegetable grown in industrially polluted and non-polluted area [7-12]. The aim of present study was to investigate the presence of heavy metals in vegetable grown near largest industrial area of Karachi i.e. Korangi Industrial Area (KIA) and to identify the causes of contamination.

Result and Discussion

Heavy metal contents in water, soil, vegetables and tomatoes of KIA samples (on dry weight basis) are shown in Table-1. In general, the results reveal that Cd, Co, Cr, Cu, Fe, Pb, Hg, Mn, Ni and Zn were found 0.039, 0.828, 0.250, 1.62, 18.8, 0.9, 0.095, 1.89, 0.245 and 1.85 mg/lit in the waste water samples and 4.85, 275.7, 64.5, 524.8, 11.40, 653.9, 2.7, 425.3, 56.2 and 265 mg/kg in the soil samples respectively. It has already reported that most of the metals gradually move down the solid profile. The rate depends on the chemicals characteristics of soils and intrinsic properties of metal [13]. The metals such as Cu and Zn and Mn reacts with soils in presence of organic matter to form chealate at pH 6.5 or above and tends to become slowly available to plants and specially they are present in high-valant or oxidizing form [14]. The water supply for the agriculture use around Karachi is negligible. Ground water in Karachi is also not feasible for regular irrigation of crops [15-16].

Cd is toxic to human in even at low concentration. The Cd contents found in Sponge gourd, spinach and tomatoes as 0.2, 1.4 and 0.9 mg/kg

Table 1: Trace Metal Contents in Water, Soil & Vegetable

Concentration (mg/kg)

	Cd	Co	Cr	Cu	Fe	Pb	Hg	Mn	Ni	Zn
Water[a]	0.039[a]	0.828[a]	0.250[a]	1.620[a]	18.80[a]	0.900[a]	0.095[a]	1.890[a]	0.245[a]	1.850[a]
± SD	0.01	0.02	0.006	0.012	0.6	0.001	0.001	0.03	0.14	0.05
Soil	4.850	275.7	64.50	524.8	11.40	653.9	2.700	425.3	56.20	265.0
±SD	0.004	0.2	0.006	0.50	6.0	0.60	0.002	0.40	0.05	0.30
Spinach	1.400	3.000	1.500	53.80	242.5	61.5	0.180	37.20	11.30	66.50
±SD	0.001	0.002	0.002	0.05	0.25	0.62	0.002	0.04	0.012	
Sponge gourd	0.200	1.600	0.800	60.30	46.3	1.65	0.950	27.90	7.000	22.80
±SD	0.001	0.002	0.001	0.06	0.04	0.001	0.001	0.03	0.007	0.02
Tomato	0.900	2.700	0.500	29.40	64.8	11.4	0.050	1.350	6.800	23.50
±SD	0.001	0.003	0.001	0.03	0.07	0.01	0.001	0.001	0.007	0.03

a: mg/lit.

respectively. It was found as 4.85 mg/kg in soil and 0.039 mg/lit in water sample. Cd is found in spinach 35 fold higher than the feed water. It also shows that cadmium accumulation from water to soil is very high (124.36 fold). Cadmium is usually present in aluminum solder, dental amalgams, storage batteries motor vehicle exhausts and cigarette smoke. The acceptable range of cadmium is 200 $\mu g/m^3$. About 6 to 10% of cadmium is absorbed in the body and transported in red blood cells. Normally it attacks on gastrointestinal system, respiratory tract cardio-vascular system, kidney, and bones. The kidney absorbs the highest concentration of cadmium and the damage of olfactory nerves is a consequence of cadmium exposure [17]. There is no health-based guidelines are available for cobalt. But its toxic side effects are observed due to its high intake available in literature [18]. The concentration of Co was found to be 0.82 mg/l in water and 275.7 mg/kg in soil, 1.6, 3.00 and 2.7 mg/kg in sponge gourd, spinach and tomatoes respectively. Accumulation of this metal into soil was observed 333 fold then water and 1.94 to 3.62 fold higher vegetable and tomato samples. This indicates a high accumulation of Co among all of the metals investigated, into soil from water. Cr found to be 0.250 mg/l in water and its accumulation in the soil were found to be 258 fold higher than the feed water. But its accumulation into the vegetable sample was observed 2-6 folds than feed water. It is found to be 0.8, 1.5 and 0.5 mg/kg in sponge gourd, spinach and tomato samples respectively. Chromium plating is one of the major uses of this metal. Steel fabrication, paint and pigment manufacturing and leather tanning constitute other major uses of chromium. Occupational exposure to chromium compounds causes dermatitis, penetrating ulcers on the hands and forearms, perforation of the nasal septum, and inflammation of the larynx and liver. The ulcers are believed to be due to chromate ion and not related to sensitization. The hexa-valent form is generally considered the most harmful causative [18]. Cu is generally regarded as a non-toxic for human, but it becomes toxic at a certain level [17]. Its concentration was found to be 1.62 mg/l in water, 524.8 mg/kg in soil and 60.3, 53.8 and 29.4 mg/kg in sponge gourd, spinach and tomatoes samples respectively. Its accumulation from water to vegetables is found to be 18.15 to 37.22 folds than feed water. Pb and Hg are considered as the toxic metals for health and they play a major role in reduction of IQ, impaired growth and hearing loss [19]. Their accumulation from feed water to vegetables was found to be 68.3 and 10 fold respectively. Nickel is responsible for lungs and nose cancer; it also affects the performance of respiratory tract, skink, liver and intestine [17]. Its accumulation from feed to soil and a vegetable (Spinach) was found to be 229.4 and 28.6 folds higher than feed water respectively.

In the previous study analysis of trace metals Cr, Fe, Pb, Zn and Hg was conducted in the industrial wastewater at different locations (Korangi Industrial Area stream and SITE stream) using standard methods of analysis. Some physicochemical parameters like pH, Phosphates, TDS, BOD and COD were also investigated. Korangi Industrial Area stream was found to contain a great amount of toxic metals. The stream was found to be bringing a lot of toxic substances along with water. The stream was also found to be one of the major sources of toxic substances for the Arabian Sea especially for Karachi coastal area [20].

This study leads to a conclusion that natural cycle of element is required for the conservation of solid fertility [21]. The nutrient may be returned to soil in admixture with the wastewater-by-wastewater treatment. Vegetables contain large amount of

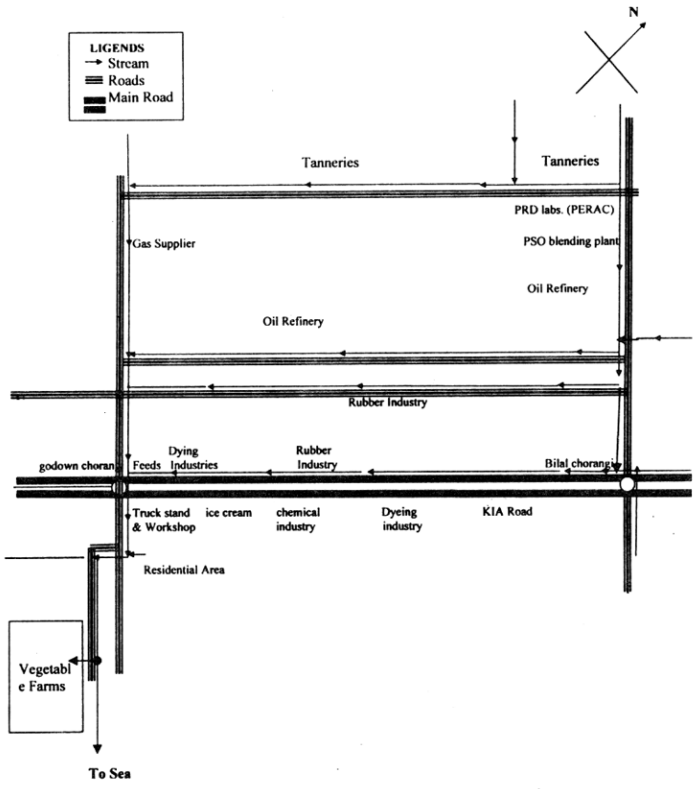

Fig.1: Korangi Industrial Area

minerals vitamins, carbohydrates, protein and fiber. The required amount of vegetables is 300-350g per person daily [22]. The vegetable, tomato, soil, and water investigated during the study were found to be contaminated with a large amount of heavy metal due to uncontrolled disposal for industrial wastewater. This metal contamination has rendered the water unusable for irrigation purpose. It is therefore essential that effective and appropriate measures may be taken and necessary regulation may be adopted to prohibit the indiscriminate discharge and disposal of industrial effluents and uses of these effluents for irrigation purpose.

Experimental

Sampling

Sampling was carried out from a vegetable farm located along KIA. At that location different vegetables and tomatoes are grown by untreated industrial water. Fresh samples of spinach (*Spinacea Oleracea*), Sponge gourd (*Luffa cylindrica*) and tomato (*Lycopercium*) were collected from the vegetable farm as shown in fig. 1. Soil samples were collected from similar location randomly at 10-60 cm depth.

Reagent and Apparatus

Perkin-Elmer 2380 atomic absorption spectrometer, equipped with standard burners and standard cathode lamp (Cathodeon®) was used for metal analysis. Pyrex glassware was washed with distilled deionized water and then with HCl-HNO_3 (1:1), again with deionized water, dried and then used for digestion. All reagents used were of analytical grade (Merck and BDH).

Procedure

(a) Soil samples were air dried at 105°C for 48 hrs, crushed in hammer mill and powdered.

(b) Vegetables and tomatoes samples were washed and cut into pieces, air dried in Fluidized Bed Dryer at 80°C for 4 hrs. The dried material was then powdered in a hammer mill. The samples of tomatoes were homogenized before air-drying.

Digestion

(a) One gram of the dried soil samples were added 10ml HNO_3-HCl (1:1) than shaken for 15 minutes and heated to dryness. 10ml HNO_3-HCl (1:1) were again added to the residue and reheated to dryness. 10ml (2N) HCl was added to the residual content and were shaken well, heated for 5 min., filtered with Whattman-42 filter paper and the filtrate was then diluted to 100 ml with double distilled water [12].

(b) Vegetable and tomato powder sample were wet digested with a little modification in the method prescribed by Anderson (1972). 2g samples were taken into digestion tube and 50 ml HCl (conc.) was added to it. The tube was then heated in digester (Tecator-2006) to dryness. After cooling 10 ml HNO_3 (Conc.) was added to the sample and heated for 30 min at 120°C and at 150°C till a clear solution was obtained. After cooling 2 ml 70% $HClO_4$ was added to the sample. Digested sample was diluted to a volume 50 ml with distilled deionized water [23].

Standard Solutions

For atomic absorption spectroscopy (AAS) Stock solution standard of (1000 ppm) were prepared by BDH Spectrosol™ AA standards. The working standard solutions were obtained after diluting the stock to the required concentrations.

Determination of Elements

The elemental concentrations in vegetable, tomatoes and soil samples were measured on a Perkin-Elmer-2380 atomic absorption spectrometer, using hollow cathode lamps (Cathodeon®) of the elements at the characteristic wavelengths. Atomic absorption data was, acquired by aspirating aqueous single element standard solutions, blank and samples, with two de-ionized water rinses between each two readings. Appropriate dilutions were made for sample solutions. APDC-MIBK (Ammonium Pyrolidine DithioCarbamate-Methyl Isobutyl Ketone) extraction and complexation method was used to determine the concentration of Cd, Co, Cr, Ni and Pb [20]. Hg was measured by cold vapor technique [24]. Detection limits of Cd, Co, Cr, Fe, Pb, Mn, Ni and Zn were found in a range of 0.002-0.5, 0.008-2.0, 0.004-2.0, 0.01-3.0, 0.007-1.0, 0.0006-0.8, 0.05-2.0 and 0.006-0.8 ppb respectively. The detection limit for Hg by cold vapor technique was found to be 0.001ppb. Metal accumulation from water to soil and water to vegetable was also determined by dividing the metal content in soil or vegetable by metal content in water.

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