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LEAD AND CADMIUM CONTAMINATION OF SOILS AND MAIZE PLANTS BY THE USE OF CONTAMINATED CANAL WATER

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ABSTRACT

Background Heavy metals are generally defined as metals with high densities, atomic weight or atomic number. In Pakistan, domestic and industrial wastewater is either discharged directly to a sewer system, natural drain, water body, nearby field or an internal septic tank. Mostly, this wastewater is not treated and none of the cities have any biological treatment facility except Islamabad and Karachi. There seems no national policy in effect on sustainable use of wastewater in the country. Some heavy metals are essential nutrients (cobalt and zinc) or harmless, but some can be toxic in larger amounts such as lead (Pb) and cadmium (Cd).

Methodology The present investigation was focused on studying the level of Pb and Cd in soil, water and plants mainly due to canal water contamination by discharging wastewater and their concentration in upstream and downstream. The canal "Al-Hammed" flowing in Multan, Pakistan was selected for study. Six crops species (*Trifolium alexanddrinum, Solanum tuberosum, Brassica, Brassica oleracea, Daucus carota* and *Zea mays*), irrigated with canal water were selected to study plant metal accumulation.

Results Significantly higher levels of Pb and Cd were found in water, plants and soil samples, especially in downstream area with respect to upstream. Compared with upstream, applying canal water on downstream raised soil Pb and Cd in both total and available forms. Through comprehensive comparison, it was found that Pb and Cd affected water quality not only where these were originated but also where end up in water system. It was suggested that Pb and Cd in canal water travelled far toward downstream. Samples collected from downstream showed higher Pb and Cd. The range of leaf Pb and Cd concentration was 0.40 to 0.98 mg kg^{-1} and 0.07 and 0.46 mg kg^{-1} on both upstream and downstream, respectively. Among all the plant species studied, *Trifolium alexanddrinum* at downstream contained maximum Pb (0.98 mg K^{-1}) and maximum Cd at downstream contained by *Solanum tuberosum* (0.46 mg K^{-1}). Total water Cd in upstream and downstream ranged between 0.02 to 0.03 mg L^{-1}. Total soil Pb value ranged between 13 to 26 mg kg^{-1}. Extractable soil Pb values ranged between 0.11 to 0.21 mg kg^{-1}. Total soil Cd ranged from 1.3 to 1.6 mg kg^{-1}. Extractable soil Cd ranged from 0.03 to 0.08 mg kg^{-1}.

Conclusion Results indicated that reasonable concentration of Pb and Cd in canal water could adversely affect soil and crops grown in downstream region and human's health due to use of contaminated vegetables.

INTRODUCTION

Heavy metals are groups of metals with density greater than 5 g cm^{-3} (Huton and Symon 1986). There are two main types of heavy metal pollution, point source and non-point source. In point source pollution, pollutants are released from discrete conveyances such as a discharge pipe. The main point source dischargers are factories and domestic waste units, which release untreated wastes. The non-point source pollution is a

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combination of pollutant from a large area rather than from specific identifiable sources. In developing countries, rapid urbanization and industrialization are the main causes of heavy metal pollution and becoming serious threat to agricultural soils (Wei and Yang 2010; Ashraf et al. 2018; ; Khan et al. 2019). When industrial and sewerage wastewater is added continuously into an irrigation canals, it may develop excessive heavy metals concentrations in canal water. Subsequently, irrigation with contaminated canal water could increase soil nitrogen (N), phosphorus (P), potassium (K) and heavy metals in soil and plants depending upon the number of years of irrigation (Mohammad and Mazahreh 2003).

Industrial water pollution is an emerging problem because there is little or no incentives for industry to treat their effluents. In Khyber Pakhtun Khawh province (formerly NWFP), 0.701 x 10^{9} m^{3}/yr of industrial effluents containing a high level of pollutants are discharged into the River Kabul (SOE 2005). In Sindh province, only two sugar mills out of 34 have installed mechanisms for wastewater treatment mainly because of international pressure as these industries (distilleries) export their products (SOE 2005). With an exception to fertilizer sector which invested significantly in installing wastewater discharge treatment plants; throughout Pakistan the industrial approach towards environment is very discouraging. In Lahore, a major city of Punjab province, only 3 out of more than 100 industries using hazardous chemicals treat their wastewater. The situation is even worst in Sindh province, for example, in Karachi, Industrial Trading Estate (SITE) and Korangi Industrial and Trading Estate (KITE), two of the biggest industrial estates in Pakistan are working with no effluent treatment plant.

In Pakistan, only 8 cities have wastewater treatment facilities, only up to primary level. According to the Pakistan water situational analysis, there are three wastewater treatment plants in Islamabad, of which only one is functional. Karachi has two trickling filters where effluents generally receive screening and sedimentation. Lahore has some screening and grit removal systems, but they are hardly functional. In Faisalabad, there is a wastewater treatment plant, in which wastewater receives primary treatment. In rural areas, wastewater treatment is nonexistent, leading to increased pollution.

Prime importance should be given to the treatment of industrial effluent before it is allowed to discharge into a drain. The environmental laws and their implementation need to be dealt more seriously and responsibly (Ensink et al. 2004). People suffered from Cd exposures through eating of unsafe food, drinking of water contaminated by substantial quantities of Cd. It is clearly understood that Cd is the major cause of osteoporosis terminated through protein deficiency (Engstrom et al. 2011). Small proteins are found in urine acting as biomarkers of kidney failure. Chronic Cd not only accumulated in the kidneys and liver but also affected the soft body tissues (Messner et al. 2009; Messner and Bernhard 2010). It resulted in increased hypertension disorders (Nawrot et al. 2008). Navas-Acien et al. (2005) suggested that Cd is involved in arteries dysfunction because this was associated with urinary and blood Cd levels.

Cadmium is non-essential element that negatively affects plant growth and development. It is recognized as extremely significant pollutant due to high toxicity and large solubility in water. Cadmium alters mineral uptake in plants through reduction in soil microbes (Das et al. 1997). As a highly toxic metal, Pb is regarded as the most common and persistent contaminant. In plants, it strongly inhibits growth, root elongation, seed germination, seedling development, chlorophyll production, transpiration and protein content (Khalid et al. 2017). In humans, it may cause very deleterious effects on nervous, hemopoietic, reproductive systems and urinary tracts (Papanikolaou et al. 2005). Plants absorb Pb along with other nutrients present in the soil. This process is controlled by many factors including soil particle size, pH, root surface area, cation exchange capacity and other physico-chemical parameters (Hadi and Aziz 2015). Its accumulation also depends upon time of exposure, concentration and climatic factors.

Heavy metal concentration is continuously increasing in Pakistan, most pollution in canals passing through the cities. Heavy metal concentration such as Pb and Cd is very high due to common practice of discharging untreated industrial, municipal and domestic wastewater into canals. However, not much importance has been given to address this serious issue. There is hardly any well-organized study which focused on risk assessment in a systematic way. Some of the systematic work has been done by IWMI and Pak-EPA with financial aid from foreign donors. Therefore, a well-coordinated program is necessary to create awareness among different sections of the society including the general public, organizations, industrialists and farmers. The present study was performed to determine the concentration of two heavy metals (Pb and Cd) in canal water, agricultural soils and plants grown with contaminated canal water.

MATERIALS AND METHODS

Site study

The Multan lies on 135 m above the sea level. The climate in Multan is called desert climate. The average annual temperature is 25.6ºC, while average rainfall is

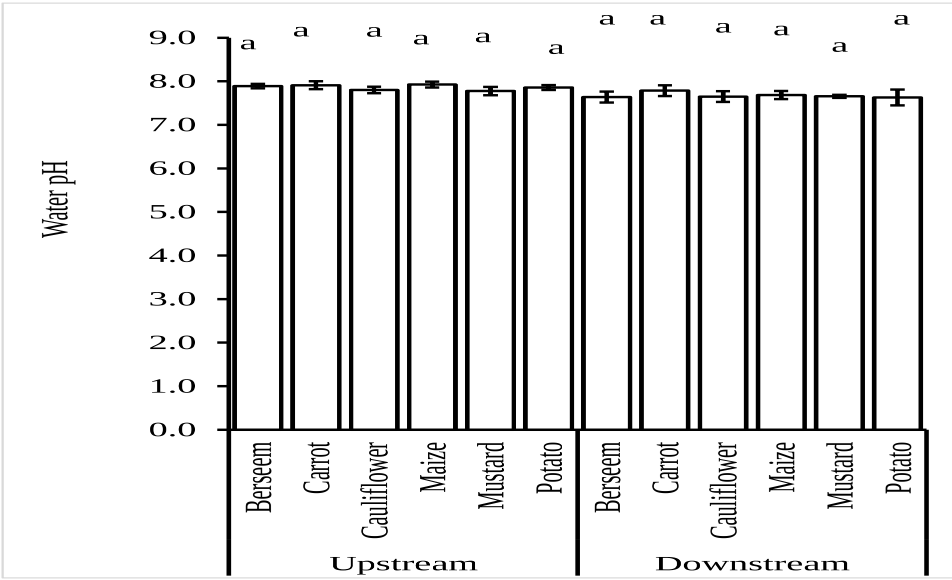

Figure 1 pH in water samples collected from upstream and downstream areas of Al Hammed canal in Multan

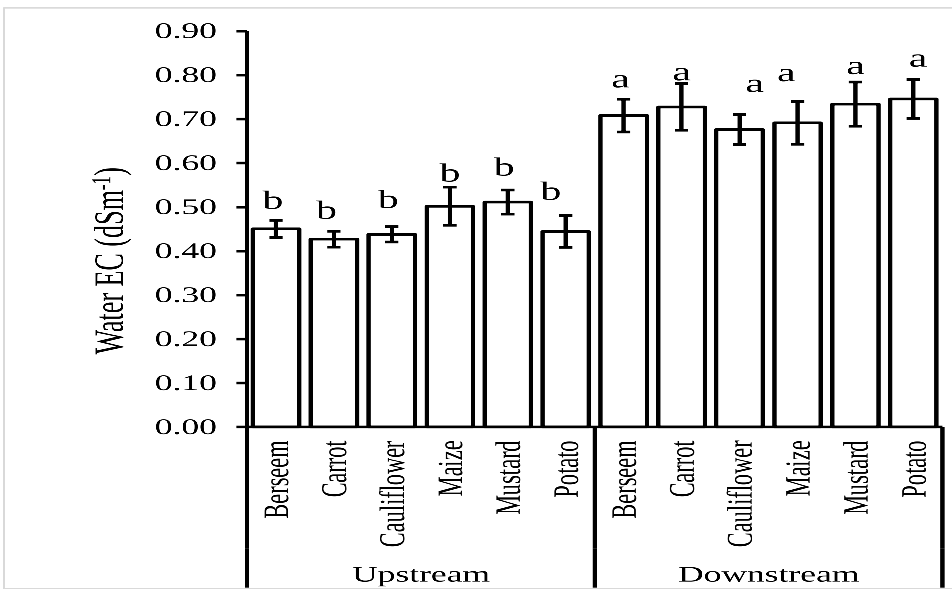

Figure 2 Water EC in samples collected from upstream and downstream areas of Al Hammed canal in Multan

175 mm. The soil was sandy loam having pH value 7.8±0.5. Being sandy in nature, the amount of organic matter and other nutrients were relatively low in soil. Multan is most important agricultural area, particularly known for cotton and mango production. Canal water is the major water source for irrigation. The study was planned to determine wastewater-induced Pb and Cd concentration in canal water, crops and soil.

Sampling strategy

The surveyed area was sub divided into upstream and downstream. Soil and plant samples were collected from two locations (upstream and downstream) irrigated with canal water. Top soil sample (0-15 cm) were collected in clean plastic bags, and random plant samples were collected in paper bags and brought to laboratory. The soil samples were air-dried, crushed to pass through 2 mm sieve, and then oven-dried at 104^0C. Soil parameters including pH, electrical conductivity (EC), organic matter (OM), soil texture, $CaCO_3$ and heavy metals (Pb and Cd) were determined using standard procedures (Richards 1954). Water samples collected from same field from where soil and plant samples were collected. Water samples were stored in clean plastic bottles in refrigerator to avoid microbial growth.

Procedure

Soil pH was determined in 1:1 suspension of water to soil by using pH meter. Buffer solutions of pH 4.5 and 9 was used to calibrate the meter. Combined-electrode was dipped into the suspension and stabilize meter reading was recorded. Metal content (Pb and Cd) in plant samples were extracted by dry ashing method (HNO_3, HCl, and H_2O_2 (Soon and Abboud 1993).

Pb and Cd determination in soil

In soil, available Pb and Cd was determined using AB-DTPA method. One gram air dry soil was put into Teflon beakers. Add 10 ml H_2O_2 and heat till dry, and then 10 ml hydrofluoric was added in a beaker and dry followed by HNO_3 and $HClO_4$ and dry. Make 50 mL volume and filter in volumetric flask. AB-DTPA extractable method was used for extractable Pb and Cd determination. Add 20 ml AB-DTPA solution and 10 g soil in Erlenmeyer flask and shook for 15 minutes. Filter the suspension through filter paper and analyze filtrate on atomic absorption spectroscopy.

Water analysis

Irrigation water samples from upstream and downstream were collected to determine Pb and Cd concentration. The water samples (about 2 L) were taken from each site and filtered. EC and pH were measured directly and then stored in stoppered clean plastic bottles. One liter water samples were gently evaporated until dryness, dissolved in 10 mL of concentrated H_2O_2 and heat to dryness. The dried material was dissolved in 10 mL hydrofluoric acid, and Pb was measured as described by Kopp and Korner (1967). Add 15 mL HNO_3 and $HCLO_4$ and heat to dry. Cool and add few drops of HCL and make volume 50 mL by adding distil water and filter in plastic bottles.

RESULTS AND DISCUSSION

Canal water characterization

All the water samples were alkaline in pH ranged from 7.6 to 7.9 (Figure 1). In upstream, water pH ranged from 7.8 to 7.9 while in downstream, water pH ranged from 7.6 to 7.8. The comparison of data between upstream and downstream areas showed that pH was higher in upstream area than downstream area. Slight variation in pH was because of effluent discharge in canal water. Zaman et al. (2018) suggested that water pH did not show any relation to water quality. Alkaline pH in this study was similar to finding of Perveen et al. (2006). Canal water EC varied from 0.43 to 0.75 dS m^{-1} (Figure 2). In upstream, EC ranged from 0.43 to 0.51 dS m^{-1} and downstream EC was observed between 0.68 to 0.75 dS m^{-1}. Average EC of water samples in upstream was 0.45, 0.43, 0.44, 0.50, 0.51 and 0.44 dS m^{-1} whereas in downstream, the average EC was 0.70, 0.73, 0.69, 0.68, 0.73 and 0.75 dS m^{-1}. Irrigation water with EC below 1.0 dS m^{-1} is considered safe for irrigation.

All water samples had measureable Cd concentration (Figure 3). On an average basis, maximum concentration was recorded in water samples collected from mustard crop from both locations. In upstream, the Cd levels ranged from 0.01 to 0.02 mg L^{-1} while in downstream, values were between 0.02 to 0.03 mg L^{-1}, highest Cd concentration was observed in downstream area compared with upstream area. The National Environmental Quality Standards 1999 limits for Cd is 0.1 mg L^{-1}, and both water samples had Cd concentration under permissible limit. Dewani et al. (1997) reported a significant amount of heavy metals in canals passing through cities. Rensink et al. (2007) observed larger amounts of heavy metals in industrial effluent. Khattak et al. (2012) found that 80% ground water samples as unfit for irrigation.

Water samples also had measureable Pb concentration (Figure 4). In upstream, Pb concentration varied from 0.06 to 0.08 mg L^{-1} and in downstream, Pb varied from 0.12 to 0.14 mg L^{-1}. The National Environmental Quality Standards (NEQS) 1999 limit for Pb in irrigation water is 0.5 mg L^{-1}. The reason for higher Pb concentration in canal water was due to discharge of untreated industrial effluents, home waste discharge and also due to air borne Pb deposition (Abo-Waly et al. 1997). It was clearly observed that those areas having greater industrial activities showed higher Pb concentration. High traffic load could also be an important factor of higher Pb concentration in canal water.

Soil characterization

Results revealed that all the sampled fields were alkaline in nature and majority of sampled fields had pH above 8.0 (Figure 5). Alkaline pH was due to arid climate, low rainfall, high temperature and alkaline parent material. The EC of soil samples varied from 0.9 to 1.4 dS m^{-1} (Figure 6). In upstream, the EC of the soil samples was between 0.9 to 1.2 dS m^{-1} and in downstream, EC in soil sample was between 1.3 to 1.4 dS m^{-1}. Results revealed that downstream area had higher EC as compared to upstream areas. Results regarding total soil Pb concentration is presented in Figure 7. It was found that soil Pb concentration was

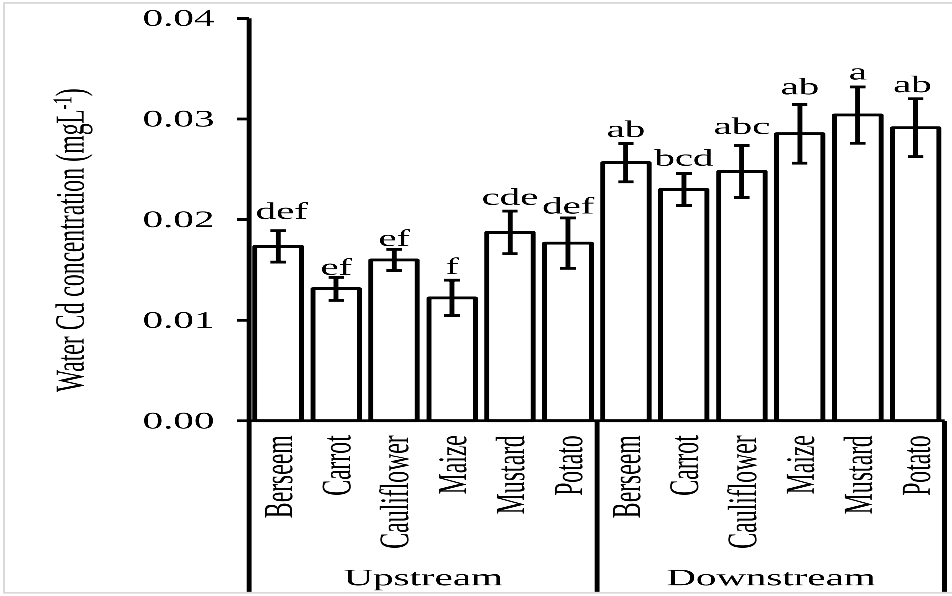

Figure 3 Water Cd concentration in water samples collected from upstream and downstream areas of Al Hammed canal in Multan

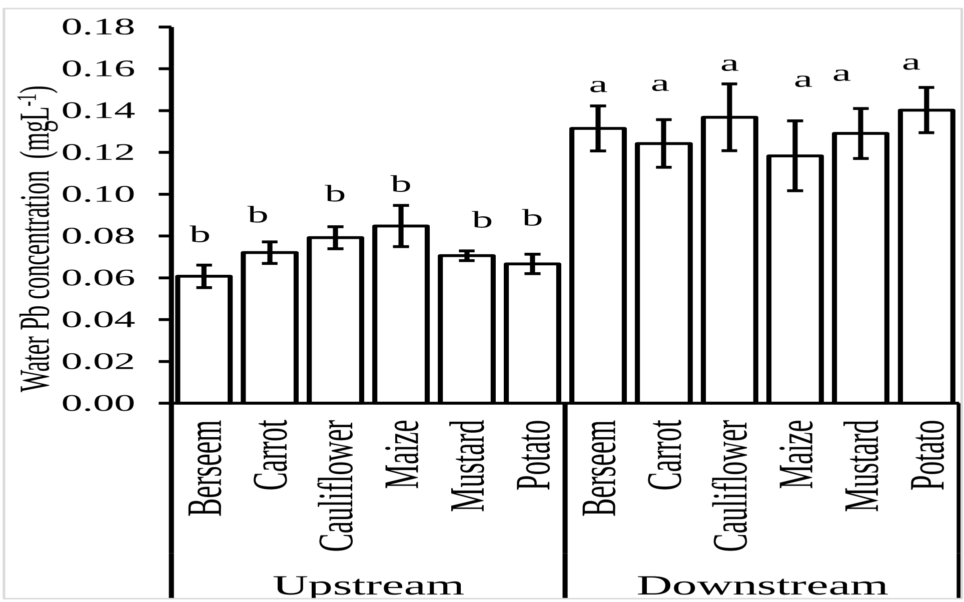

Figure 4 Water Pb concentration in water samples collected from upstream and downstream areas of Al Hammed canal in Multan.

directly proportional to its contents in water. In upstream, soil samples contained total Pb concentration in the range of 13 to 19 mg kg^{-1} while, downstream values ranged from 22 to 26 mg kg^{-1}. The Pb concentration in upstream and downstream areas were below the permissible limit. Industrial activities such as paints and battery manufacturing contributed metal deposition in soil. Manures and atmospheric deposition could also add significant quantities of metals in soils (Wei and Yang 2010). The mean values for extractable soil Pb concentration in soils are given in Figure 8. It ranged from 0.11 to 0.21 mg kg^{-1} on both upstream and downstream areas. Soil sample collected from potato soil showed higher Pb in both upstream and downstream areas. Similar results were reported by Rattan et al. (2005).

The mean values of total soil Cd concentrations in soil studied are given in Figure 9. The significant difference were found between upstream and downstream areas. In upstream area, Cd concentration

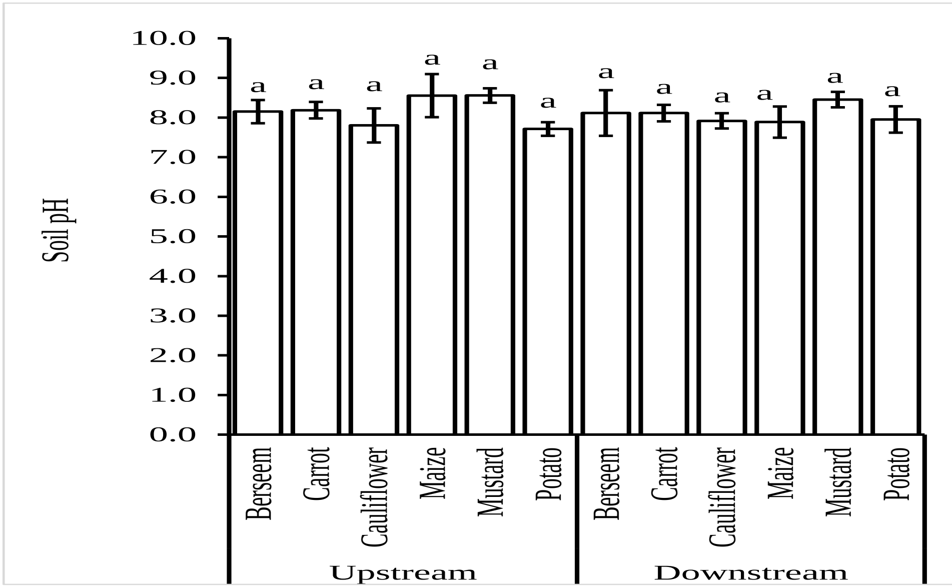

Figure 5 Soil pH in samples collected from upstream and downstream areas of Al Hammed canal in Multan

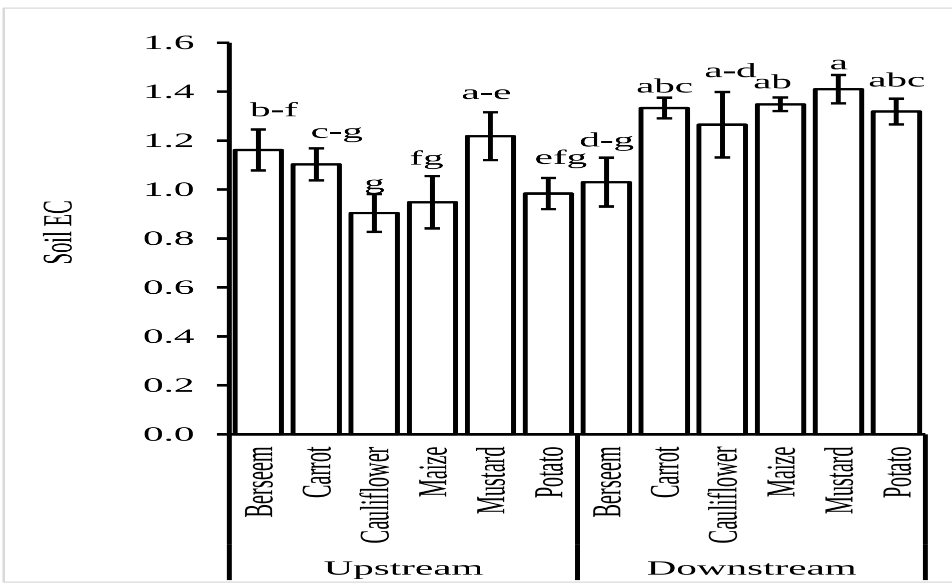

Figure 6 Soil EC in samples collected from upstream and downstream areas of Al Hammed canal in Multan

ranged from 1.0 to 1.3 mg kg^{-1}, and the downstream values varied from 1.6 to 2.2 mg kg^{-1}. Mean extractable soil Cd concentration detected in upstream soil ranged from 0.02 to 0.03 mg kg^{-1} while, downstream area, concentration varied between 0.05 to 0.08 mg kg^{-1} in downstream area (Figure 10). The reason for high extractable Cd in downstream could be due to discharge of industrial wastewater in clean canal water.

Leaf metals concentration

The mean concentration of Cd in leaf samples in upstream area was 0.19, 0.12, 0.16, 0.07, 0.16 and 0.19 mg kg^{-1} while, in downstream area, the mean Cd concentration were 0.43, 0.34, 0.40, 0.26, 0.41 and 0.46 mg kg^{-1} (Figure 11). A comparison of Cd concentration in leaf tissues revealed that leaf Cd was higher in downstream area than upstream area. Cadmium concentration in leaf and other edible parts of crops used for human consumption and for forage purposes depends on number of irrigations per year. Crops irrigated with canal water, tube well and sewage water for long period of time showed more metal levels as compared to such crops irrigated with contaminated water for short time (Ismaila et al. 2014) Leaf Pb concentration in upstream area were 0.40,

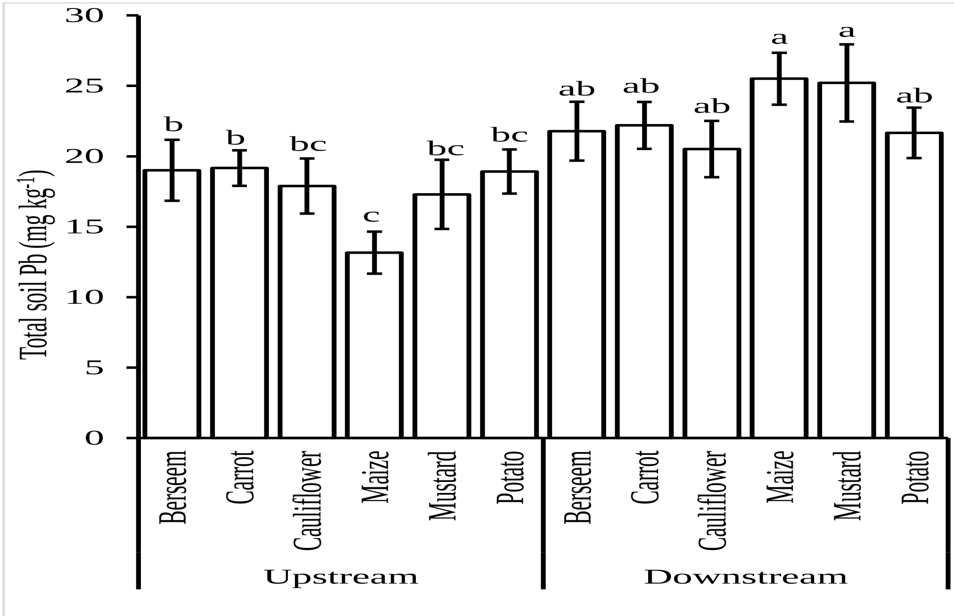

Figure 7 Total soil Pb in samples collected from upstream and downstream areas of Al Hammed canal in Multan

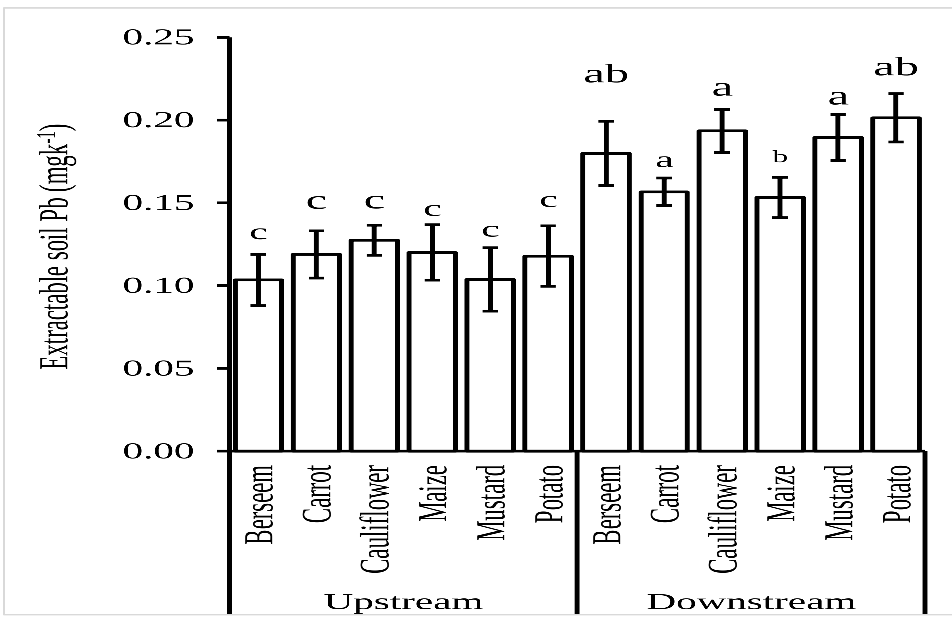

Figure 8 Extractable soil Pb contents in samples collected from upstream and downstream areas of Al Hammed canal in Multan

0.23, 0.35, 0.15, 0.28 and 0.56 mg kg^{-1} while 0.98, 0.65, 0.95, 0.43, 0.72 and 1.11 mg kg^{-1} in downstream area (data not shown). In both upstream and downstream areas, maximum Pb was found in leaves of potato and minimum in maize. Furthermore, leaf samples from downstream area had more Pb concentration than upstream. The data from this study compared with Kabata-Pendias and Pendias (1985) showed Pb concentration was above than permissible limit. According to Singh et al. (2010), Pb was higher in irrigation water, lower in soil but higher in vegetables than WHO limits. It was found that Pb was low in irrigation water, higher in plants than safe level when plants were grown with contaminated water (Gupta et al. 2010).

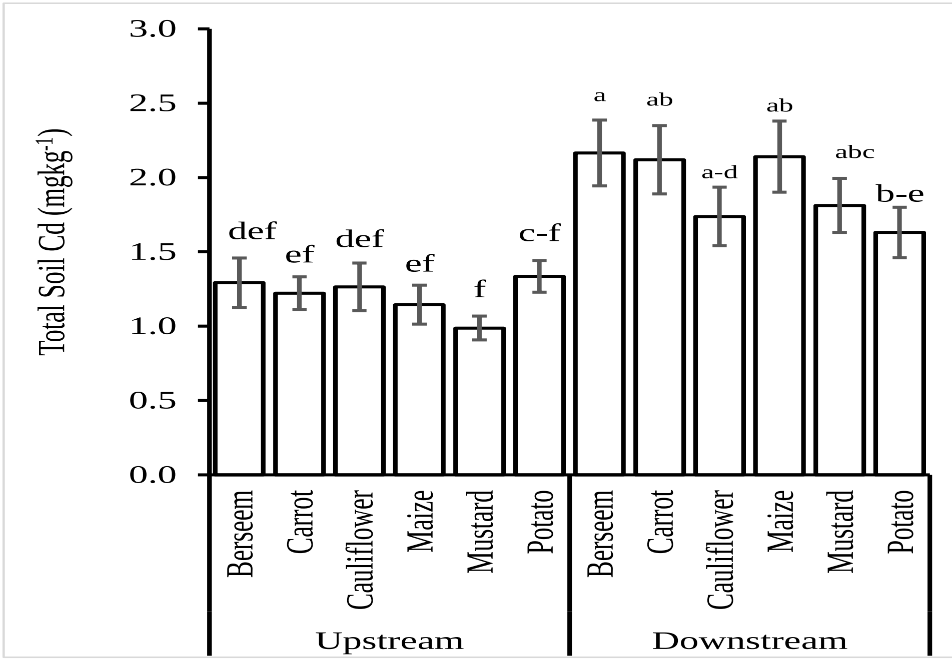

Figure 9 Total soil Cd contents in upstream and downstream areas of Al Hammed canal in Multan

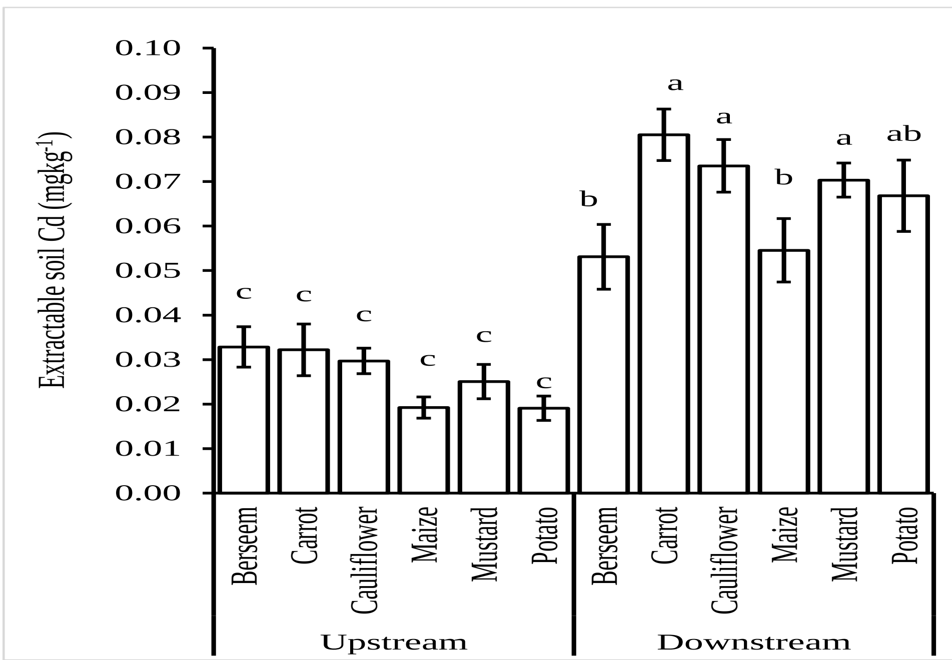

Figure 10 Extractable soil Cd concentration in all soil samples collected from upstream and downstream areas of Al Hammed canal in Multan study area.

CONCLUSIONS

It was found that Pb and Cd concentrations were found in all soil, water and plants samples investigated. Heavy metal concentrations were higher in downstream areas than upstream areas. Downstream region contained high Pb and Cd concentrations due to industrial activities. Municipal sewage water discharged into canals without treatment caused higher metals accumulation in downstream. In upstream at the point from where samples collected, many industrial activities were carried out behind that point which were the main reason for canal water contamination.

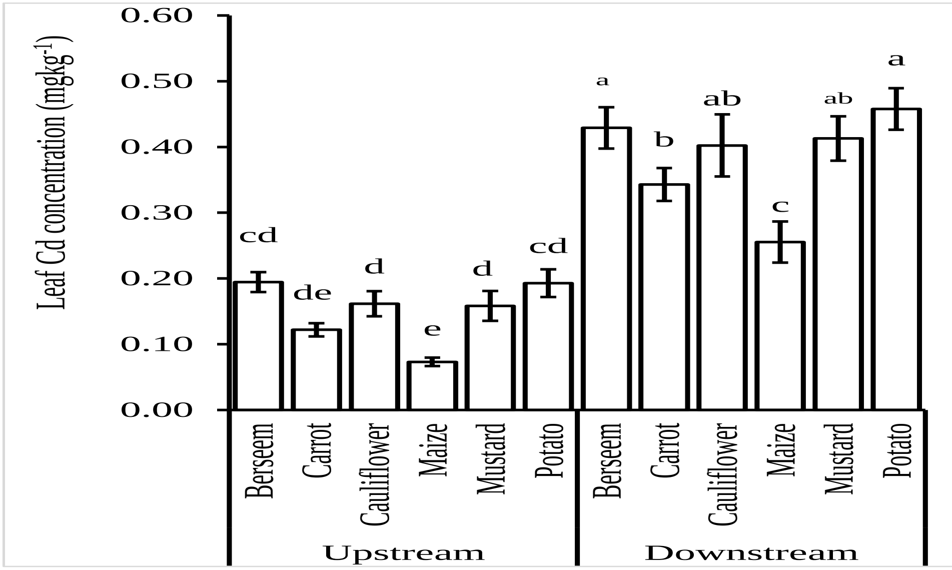

Figure 11 Leaf Cd concentration in upstream and downstream areas of Al Hammed canal in Multan

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