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Detection of Some Heavy Metals Due to Sewage Water Diffusion into Planted Land

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Abstract: The concentrations and transfer factor of some heavy metals including copper (Cu), zinc (Zn), silver (Ag), lead (Pb), mercury (Hg) and cadmium (Cd) in some fruit and leaves of plants grown in the polluted soil of Um Al Nasser village were determined using atomic absorption spectroscopy. The study showed a significant pollution of plants with some of the studied metals which exceeded in some cases the allowed values approved by WHO and FAO. The concentrations of copper, zinc, silver, lead and mercury were in the range: 0-14.5 , 5.9-115.4, 0-1.8, 0- 68.0 and 7.3-29.6 $\mu g\ g^{-1}$, respectively. No significant amount of cadmium was detected. Transfer factor was varied amongst the plants and also amongst the species of the metals.

Key words: Heavy metal, wastewater pollution, health risk trace elements contamination, atomic absorption spectroscopy

INTRODUCTION

Human life could be at risk of adverse health effects from consuming plants grown in a polluted environment containing elevated metal concentrations. These plants can accumulate these metals and hence enter the food chain in significant amounts (Kabata-Pendias and Pendias, 2000; Alloway *et al*., 1990). The widespread of contamination with heavy metals in the last decades has raised public and scientific interest (Kumar, 2004; Gilbert, 1984). Heavy metals are given special attention throughout the world due to their toxic effects even at very low concentrations (Loska *et al*., 2000; Chibowski, 2000; Solecki and Chibowski, 2000; Islam *et al*., 2007). Some researchers studied the pollution with heavy metals in air, water and foods to avoid or reduce their harmful effects and to determine their permissibility for human consumption (Zakrzewski, 1997; Queirolo *et al*., 2000). The use of samples that may be contaminated with heavy metals in food may result in accumulation of these metals in human organs and lead to different health problems (Sekhar *et al*., 2002; Boon *et al*., 1992; Calabresse *et al*., 1997).

Previous studies have also shown that heavy metals are potentially toxic to crops, animals and humans when contaminated soils are used for crop production (Xian, 1989). Heavy metals may enter the human body through inhalation of dust, consumption of contaminated drinking water, direct ingestion of soil and consumption of food plants grown in metal-contaminated soil (Cambra *et al*., 1999; Dudka and Miller, 1999). These metals may reach and contaminate plants, vegetables, fruits and canned foods through air, water and soil during cultivation (Kennish, 1992; Queirolo *et al*., 2000; Husain *et al*., 1995) and also during industrial processing and packaging (Massanyi *et al*., 2001). Several studies were done to determine the concentration of heavy metals in samples, dry fruits and plant and to study their dangerous effects (Gilbert, 1984; Kennish, 1992; Queirolo *et al*., 2000).

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Copper and zinc are known to be essential and may enter the food materials from soil through environmental contamination (Prasad and Oberleas, 1976). The adult human body contains about 1.5 to 2 mg kg^{-1} of copper (Dente and Hopkins, 2004) and 33 mg kg^{-1} of zinc (Fairweather-Tait, 1998). Lead and cadmium are toxic and exceeding threshold values can affect human health (Steenland and Boffetta, 2000; Schwartz and Isildinha , 2000). Chronic exposure to mercury may result in permanent damage to the central nervous system (Pamphlett *et al*., 1997) and kidneys. Mercury can also cross the placenta from the mother's body to the fetus and accumulate, resulting in mental retardation, brain damage, cerebral palsy, blindness, seizures and inability to speak (Tsoumbaris and Tsoukali-Papadopoulou, 1994).

The pollution was caused due to destruction of the northern Gaza sewage wastewater basin in March 2007. The aim of this study was to determine the concentrations and transfer factor of some heavy metals such as Cu, Zn, Ag, Cd, Hg and Pb in some plants grown in the polluted area of Um Al Nasser village, Gaza, Palestine. This study was undertaken to determine levels of contamination of these toxic metals in fruits and leaves of different plants grown in the polluted area.

MATERIALS AND METHODS

The field study tool place in the Um Al Naser Bedouin village, around 20 km North of Gaza City (33.31 N latitude and 30.34 E longitude, elevation of 42 m a.s.l) Palestine. The sewage basin of Um-Al-Nasser village was expanded in 1991 to increase its peak flow capacity. The combination of an ever increasing volume of waste and insufficient capacity led to effluent overflowing the original filtration basins into the surrounding sand dunes gradually creating a large lake that by 2007 covers more than 44.5 ha (in 1995 overflow had already affected 5.3 ha). On the 27th March 2007 a basin of sewage burst its reservoirs and flooded part of Um-Al-Naser Bedouin village. Apart from direct life and property losses the village was literally swimming in waste. As a future direct consequences of the event there is a strong contamination of the soil by heavy metals. The secondary results are contaminations of plants growing in this area.

Sample Collection

Twenty five samples of leaves and twenty five samples of fruits of five different plants: Loquat (Eriobotrya japonica), Apricot (*P. armeniaca*), Peach (*P. persica*), Grapes (*Vitus vinifera*) and Raspberry (*Rubus idaeus*) of Um-Al-Nasser village area were investigated for metals contamination. Samples of these plants were collected from different sites to cover all the polluted geographical area during June-August 2007. At each site, five different leaves and five different fruits were randomly chosen for sampling. Control plants were collected from uncontaminated soil. Leaves and fruits were separated and then thoroughly washed including a final rinse with deionized water and kept in a freezer at -18°C until running analysis. Soils were also collected from the different sites and uncontaminated area at depth 0-15 cm. Soil samples were mixed, dried and sieved through 2 mm sieve.

Sample Preparation

In the investigated plant samples (Intawongse and Dean, 2006), a suitable amount, 25 g, of each sample was sun dried and oven dried at 200°C using drying oven, milled and weighed. Samples were burned gradually up to 700°C for 2 h in a muffle furnace. Ash samples were weighed after being burned and powdered. Two milliliter of concentrated nitric acid were added to samples ash for digestion. The digested samples were mixed by deionized water, filtered and diluted to 100 mL. Heavy metals were extracted from soil samples using aqua regia solution (1 mL HNO_3 and 3 mL HCl). The content was heated on a hot plate to dryness, allowed to cool, diluted with distilled water, filtered and completed to 100 mL. Samples were prepared in triplicate. A blank digestion solution was made for comparison.

A standard solution for each element under investigation was prepared and used for calibration. Plant uptake of heavy metals was expressed as proportion of heavy metals in plant tissue per tissue dry weight and transfer factor was expressed as the ratio of the heavy metal concentration in plants to that of soil.

Analytical Technique

Concentrations of the heavy metals were measured in plant samples by a Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrometer, double beam and deuterium background correction. Hollow cathode lamps of Cu, Zn, Ag, Cd, Hg and Pb were used at specific wave length of every metal. Detection limits were calculated using the expression (3S/b) were S is the standard deviation of at least five replicates of blanks and b is the slope of the calibration curve. Typical detection limits were 0.035, 0.016, 0.010, 0.020, 0.012 and 0.015 μg mL^{-1} for Cu, Zn, Ag, Hg, Pb and Cd, respectively. Difference between metal concentration and transfer factor were compared using paired t-test and the variance ratio F-test. A $p<0.05$ was considered to be the level of significant.

RESULTS AND DISCUSSION

The values of metal concentrations were compared with the maximum permissible concentration of the studied metal ions as recommended by Codex Alimentarius Commission and SEPA (2005). The mean heavy metal concentrations in some polluted plants are significantly higher than the recommended values by FAO and SEPA (Table 1, 2). Results from present and earlier studies

Table 1: Mean concentration of Cu, Zn, Ag, Hg, Pb and Cd in the leaves of different plant samples determined by AAS

Leaves	Concentrations (μg g^{-1})±SD					
sample ID	Cu	Zn	Ag	Hg	Pb	Cd
Loquat (1)	7.67±0.33	7.89±0.54	ND	ND	10.95±1.22	ND
Apricot (1)	ND	18.27±1.27	ND	ND	16.61±1.37	ND
Peach (1)	ND	14.46±1.04	ND	ND	17.05±2.43	ND
Grapes (1)	ND	30.65±2.76	ND	ND	19.13±2.37	ND
Raspberry (1)	ND	40.17±3.25	ND	ND	17.58±2.61	ND
Loquat (2)	ND	18.34±0.99	ND	ND	10.39±0.92	ND
Apricot (2)	ND	25.39±1.27	ND	ND	23.46±1.02	ND
Peach (2)	ND	15.67±0.78	ND	ND	10.78±0.73	ND
Grapes (2)	ND	36.28±2.47	ND	ND	21.41±0.96	ND
Raspberry (2)	ND	16.44±1.13	ND	ND	12.68±0.65	ND
Loquat (3)	ND	20.31±1.71	ND	ND	9.68±0.45	ND
Apricot (3)	ND	34.47±2.78	1.32±0.22	ND	17.78±1.37	ND
Peach (3)	ND	36.21±2.31	0.42±0.05	ND	24.96±2.16	ND
Grapes (3)	ND	36.70±3.21	0.43±0.03	1.92±0.30	23.19±2.22	ND
Raspberry (3)	ND	46.44±2.89	0.25±0.01	ND	18.85±1.36	ND
Loquat (4)	ND	13.93±0.34	0.066±0.01	ND	8.44±0.57	ND
Apricot (4)	ND	47.63±1.69	0.26±0.02	ND	14.73±0.87	ND
Peach (4)	ND	21.83±1.21	0.029±0.01	ND	7.26±0.55	ND
Grapes (4)	ND	85.03±4.55	0.25±0.01	1.57±0.20	24.81±1.34	ND
Raspberry (4)	ND	115.44±5.19	0.44±0.02	2.22±0.40	29.65±2.46	ND
Loquat (5)	ND	38.64±2.22	0.16±0.01	0.48±0.02	12.95±1.03	ND
Apricot (5)	ND	23.55±1.34	0.15±0.02	28.05±3.11	20.11±1.65	ND
Peach (5)	ND	22.59±1.79	0.09±0.01	35.13±3.36	24.08±1.79	ND
Grapes (5)	ND	23.79±2.11	0.11±0.01	27.76±2.47	17.63±0.78	ND
Raspberry (5)	ND	18.41±0.98	0.14±0.02	27.08±2.22	16.97±0.81	ND
Loquat (control)	1.22±0.33	25.91±0.99	ND	ND	ND	ND
Apricot (control)	3.77±0.65	28.29±2.04	ND	ND	ND	ND
Peach (control)	1.13±0.29	27.64±1.37	ND	ND	ND	ND
Grapes (control)	1.75±0.37	28.61±1.76	ND	ND	ND	ND
Raspberry (control)	4.43±0.59	43.69±2.23	ND	ND	ND	ND

ND: Not detected, SD: Standard deviation of triplicate measurements, Tabulated t-value at 95% confidence limits is 4.30

Table 2: Mean concentration of Cu, Zn, Ag, Hg, Pb and Cd in the fruits of different plant samples determined by AAS

Fruits sample ID	Concentrations (μg g^{-1}))±SD					
	Cu	Zn	Ag	Hg	Pb	Cd
Loquat (1)	ND	19.23±1.33	0.097±0.01	20.00±1.76	12.43±1.01	ND
Apricot (1)	ND	20.97±1.71	0.14±0.05	20.26±1.31	12.38±1.21	ND
Peach (1)	ND	51.31±3.45	0.50±0.04	17.85±1.37	10.07±0.97	ND
Grapes (1)	ND	94.96±5.96	1.41±0.03	49.86±3.62	27.33±1.37	ND
Raspberry (1)	ND	68.11±3.47	0.68±0.02	23.60±1.98	13.16±0.78	ND
Loquat (2)	ND	37.53±3.31	0.83±0.02	22.65±1.27	10.86±1.22	ND
Apricot (2)	ND	6.65±0.51	1.06±0.03	44.20±3.23	19.26±1.37	ND
Peach (2)	ND	58.64±2.78	0.81±0.01	36.98±3.63	20.08±1.97	ND
Grapes (2)	4.36±0.66	34.94±2.12	0.41±0.02	32.74±1.98	17.14±1.26	ND
Raspberry (2)	14.49±1.32	51.53±3.07	0.18±0.01	41.64±2.43	22.67±1.75	ND
Loquat (3)	0.53±0.06	39.99±2.42	0.90±0.01	23.75±1.77	12.88±1.09	ND
Apricot (3)	ND	5.91±0.47	0.71±0.02	68.02±3.52	27.33±1.66	ND
Peach (3)	ND	44.58±3.79	0.33±0.01	27.78±1.74	14.77±0.99	ND
Grapes (3)	ND	103.14±5.98	0.36±0.02	52.66±2.98	26.47±2.05	ND
Raspberry (3)	ND	27.56±2.01	0.18±0.01	31.99±1.97	15.69±1.29	ND
Loquat (4)	ND	48.57±3.52	0.062±0.01	24.97±1.65	11.90±0.89	ND
Apricot (4)	ND	72.67±4.11	0.089±0.01	42.79±3.09	20.81±1.27	ND
Peach (4)	ND	68.054±3.93	0.089±0.01	42.65±3.15	20.99±1.98	ND
Grapes (4)	ND	61.59±4.21	1.14±0.03	44.05±2.65	20.79±1.45	ND
Raspberry (4)	ND	60.17±3.96	0.31±0.01	53.22±3.17	23.84±1.67	ND
Loquat (5)	1.93±0.15	36.31±2.38	0.52±0.01	23.98±1.66	10.77±0.78	ND
Apricot (5)	4.71±0.70	49.88±2.34	1.15±0.23	37.49±2.19	17.21±1.65	ND
Peach (5)	1.36±0.50	15.41±1.12	0.55±0.01	20.60±0.98	9.36±0.97	ND
Grapes (5)	1.41±0.47	70.13±4.76	1.78±0.22	64.29±3.51	28.77±1.33	ND
Raspberry (5)	5.49±0.44	39.57±2.67	1.60±0.23	36.71±2.73	17.69±1.15	ND
Loquat (control)	4.04±0.31	44.47±3.79	ND	ND	ND	ND
Apricot (control)	1.71±0.22	27.12±2.17	ND	ND	ND	ND
Peach (control)	1.65±0.27	24.29±1.65	ND	ND	ND	ND
Grapes (control)	3.76±0.73	33.11±1.78	ND	ND	ND	ND
Raspberry (control)	3.91±0.61	37.47±2.26	ND	ND	ND	ND

ND: Not detected, SD: Standard deviation of triplicate measurements, Tabulated t-value at 95% confidence limits is 4.30

(Muchuweti *et al*., 2006; Sharma *et al*., 2007) demonstrate that the plants grown on the polluted soils contaminated with heavy metals and pose a major health concern.

Table 1 and 2 indicate that individual plant types differ in their metal uptake. The copper uptake was slightly low in loquat and grapes fruits, but relatively higher in raspberry and apricot. Zinc uptake was significantly higher in raspberry and grapes leaves and slightly lower in loquat and peach. Silver and mercury tended to be taken up least by all the plants studies. Cadmium was not detected in all studied samples.

The concentration of copper is found to be in the range 0-14.5 mg kg^{-1} (Table 1, 2). Comparing with standard limit, the Raspberry (2) fruit sample has the highest content of copper (14.5 mg kg^{-1}) that exceeds the standard level recommended by FAO/WHO (10 mg kg^{-1}) (2003).

The values of Zn concentrations were in the range 5.9 -115.4 mg kg^{-1} (Table 1, 2). Comparing with standard limit, the Raspberry (4) leaves sample has the highest content of zinc (115.4 mg kg^{-1}) that exceeds slightly the standard level recommended by FAO/WHO (100 mg kg^{-1}) (2003).

The values of silver concentrations were in the range 0-1.8 mg kg^{-1} (Table 1, 2). Comparing with standard limit, the Grapes (5) fruit sample has the highest content of silver (1.8 mg kg^{-1}) that highly exceeds the standard level recommended by FAO/WHO (0.005 mg kg^{-1}) (2003).

As shown in Table 1 and 2 the concentrations of mercury of many samples under investigation were upper the maximum permissible concentration of mercury (0.10 mg kg^{-1}) recommended by FAO/WHO (2003). The amount of mercury was in the range 0-68.02 mg kg^{-1}. Highest value was found in Apricot (3) fruit sample.

The lead contents of different samples are given in Table 1 and 2. As comparing with standard limit, content of lead range was 7.26- 29.65 mg kg^{-1} that far exceeds the standard level recommended

Table 3: Ratio of concentration of metals in plants leaves to soil

	Transfer factor values					
Species	Cu	Zn	Ag	Hg	Pb	Cd
Loquat	0.0216	0.0399	0.0269	ND	0.1064	ND
Apricot	ND	0.1267	0.0209	0.0423	0.1882	ND
Peach	ND	0.0447	0.0065	0.0529	0.1489	ND
Grapes	ND	0.0857	0.0095	0.0418	0.2155	ND
Raspberry	ND	0.0905	0.0101	0.0408	0.1923	ND

ND: Not detected

Table 4: Ratio of concentration of metals in plants fruits to soil

	Transfer factor values					
Species	Cu	Zn	Ag	Hg	Pb	Cd
Loquat	0.0278	0.0733	0.0175	0.0347	0.1195	ND
Apricot	0.0132	0.0629	0.0229	0.0641	0.1969	ND
Peach	0.0038	0.0960	0.0165	0.0439	0.1528	ND
Grapes	0.0081	0.1223	0.0371	0.0733	0.2099	ND
Raspberry	0.0281	0.0809	0.0201	0.0564	0.1429	ND

ND: Not detected

by FAO/WHO (0.30 mg kg^{-1}) (2003). Sample of Raspberry (4) leaves sample contained the highest concentration of lead (29.65 mg kg^{-1}). As shown in Table 1 and 2, no cadmium was detected in all samples.

The transfer factor was shown in Table 3 and 4 which expressed as the ratio of the concentration of the metals in plants to that in soil according to the method by Intawongse and Dean (2006). The higher the value of the transfer factor the more uptake the metal is. The results indicate that the transfer factor values for Cu, Zn, Ag, Hg, Pb and Cd varied among the plants and among the species of the heavy metals. The least transfer factor was recorded on Ag. It varied from 0.0065 for peach leaves to 0.0371 for grapes fruits. The Pb recorded the highest transfer factor value which ranged from 0.1064 for loquat leaves to 0.2099 for grapes fruits. The transfer factor in this study is an indication of the potentials of the heavy metals to be transferred into the food chain through the consumption of edible plants by either animals or mankind.

CONCLUSION

In conclusion, this study has revealed very high concentrations of lead, silver and mercury heavy metals in most samples planted in the Um Al Nasser polluted area. High concentrations of copper and zinc in two types plants samples were also detected. No detection of cadmium was found. The transfer factor indicated the potentials of the heavy metals to be transferred into the food chain through the consumption of edible plants by either animals or mankind. These findings are indicative of serious pollution of this area due to destroying of sewage basins. In view of these results, there is an important oblige to treat the polluted environment under review and put in place appropriate checks and balances to preserve the health of communities within the vicinity of the polluted area, particularly as the effects of heavy metals are bioaccumulative and pose great dangers to the health of humans, animals and plants.

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