The Concentration of Cd, Cu, Pb, and Zn Heavy Metals in Plants Along the Highway Between Ramtha and Mafraq

Khaled Abdu Al-Khaza'leh
Department of Physics, Faculty of Sciences, Al al-Bayt University, PO box 25113, Mafraq, Jordan

Abstract
The contamination of plants with heavy metals is a serious environmental problem. Existence of heavy metals in animal or human body over risk levels is toxic and causes different diseases. In this study, the concentration of four heavy metals; cadmium Cd, copper Cu, lead Pb and zinc Zn, in four wild plants is investigated at four different sites (10km apart) along the highway between Ramtha city and Mafraq city along the northern borders of Jordan with Syria. These plants are Stipa gigantean or Stipa grass, Trifolium resupinatum (Nafal), Anabasis aphylla (Ashnan) and Anabasis_setifera (Sheran). The results show that the investigated plants have high contamination levels by these metals at three sites, while the fourth site has lower concentration level than the others.
Keywords: Heavy metals, risk level, contamination.

1. Introduction

Mining, Industrial production, and transportation, release high amounts of heavy metals to the biosphere including plants. The probability of contamination of crop plants by heavy metals increases through the soil root interface. The heavy metals like, Cd and Pb do not essentially affect the growth of plant, but they are taken up and accumulated by plants in toxic forms. Ingestion of plants grown in environments contaminated with heavy metals considered a risk to human health and wildlife (Nazir et al. 2015) . A remarkable metal contamination is caused by vehicle emission to the neighbouring roadside ecosystem. Lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn) and other heavy metals are included in petrol, tires, oils and galvanized parts of the vehicles (Falahi 1984; Shaikh et al. 2006; Moreki et al. 2013). Heavy metals have been reported to be serious toxic. Grasses growing by the road sides can be contaminated by heavy metals emitted by vehicles. These grasses are grazed on by animals or harvested as fodders (Ellen et al. 1990). Parkpian et al. 2003 found that plants that grow nearer to the highways are usually exposed to more heavy metal accumulation than those away from highways.

Heavy metal concentration in the soil solution plays an important role in controlling metal bioavailability to plants. Most of the studies show that the use of waste water contaminated with heavy metals for irrigation over long period of time increases the heavy metal contents of soils above the permissible limit. Ultimately, increasing the heavy metal content in soil also increases the uptake of heavy metals by plants depending upon the soil type, plant growth stages and plant species (Warmate et al. 2011)

ATSDR September 2012 (Agency for Toxic Substances and Disease Registry) reported that Anemia, liver disease, and nerve or brain damage have been observed in animals eating or drinking cadmium. Kidney and bone effects have also been observed in laboratory animals ingesting cadmium. Smelting operations, coal and oil-fired boiler, phosphate fertilizer manufacture, and municipal and sewage sludge incinerators (ATSDR October 2012).

Copper can have a toxic effect on the body and mind and it is a contributor to many chronic illnesses and mental disturbances. However, copper usually affects the nervous system, the female and male reproductive system, connective tissues such as hair, skin and nails and organs like the liver (Ashish et al. 2013).

Acute exposures to lead may cause gastrointestinal disturbances, hepatic and renal damage, hypertension and neurological effects that may lead to convulsions and death (Lead 1995)

Manifestations of overt toxicity symptoms such as nausea, vomiting, epigastric pain, lethargy, and fatigue will occur with extremely high zinc intakes (Fosmire 1990).

The research sites are located along the highway between Ramtha and Mafraq. The highway usually faces heavy traffic, especially trucks, crossing the borders to and from Syria, Iraq and Saudi Arabia.. This study was undertaken to investigate the levels of heavy metal in some plants grown at both sides of the highway.

2. **Materials nad Methods**

2.1 Sampling

Four types of plants were harvested during spring season in April. The plants were Stipa Grass, Nafal, Ashnan and Sheran figures 1,2,3 and 4 respectively. The plants were from both sides and from the median of the highway. The harvested plants were classified and kept in a ventilated dry place.

Figure 1: Stipa gigantean or Stipa grass

Figure 2:Trifolium resupinatum (Nafal)

Figure 3: Anabasis aphylla (Ashnan)

Figure 4: Anabasis_setifera (Sheran)

2.2 Sample Preparation Procedure

The samples were prepared in the Analytical Chemistry Section in Jordan Atomic Energy Commission (JAEC), and prepared according to Standard Operation Procedure (SOP3) for sample preparation as follows:

2.3 Sample Preparation Procedure

The samples dried overnight at 105ºC and the moisture was calculated then; 0.25± 0.0001g was accurately taken from each sample.1.3ml concentration HF (Analytical Grade (48%)), 8ml concentration HNO_3 (Analytical grade (65%)) and 2ml H_2O_2 (Hydrogen Peroxide (30%)) were added to the samples.

The samples were digested using Milestone ETHOS1, microwave digestion system.

The samples then transferred volumetrically to 50 ml centrifuge test tube at room temperature.

Next the samples were treated with 4% boric acid to eliminate the excess of HF. NF 1200 Centrifuge System was used for samples clarification. The Samples then diluted to 50 ml as a last step in the primary chemical preparation.

The samples were diluted additionally with 1% sub boiled Nitric Acid (HNO_3 65%) 2 times as dilution factor, so the last dilution volume is 100 ml, for ICP-MS measurements.

Analytical Technique Measurement. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used in order to determine the concentration of the elements. Six calibration Standards from Accutrace Reference Standard were prepared for all interested elements. A blank was also prepared in 1% sub-boil Nitric Acid 65 % (HNO_3). Y, In and Tb were used as internal standard. Bruker 810/820 -Mass Spectrometer was used for samples measurements in order to determine the concentration of (Cd, Cu, Zn and Pb) elements.

3. Results and Discussion

Heavy metals were measured in four brands of plants taken from four different sites along the road between Ramtha and Mafraq. The concentrations were in (ppm) part per milliom, where ppm is equivalent to mg/kg unit. The risk concentration level of studied elements as reported by the ATSDR are [Pb 0.3µg/kg/day, cadmium Cd is 0.1 µg/kg/day, copper Cu 0.01 mg/kg/day, Zinc Zn 0.3 mg/kg/day (per kilogram of weight of the animal). If the average weight of a lamb is 40kg and it can eat an average of 1kg of crops per day, then risk level of these elements in ppm or mg/kg will be as follows 0.012 for Pb, 0.004 for Cd, 0.4 for Cu and 12 for Zn. So, the concentrations in the tables below will be compared with these concentrations.

Table 1. The concentration of heavy metals at site 1 (near Ramtha City)

Type	**Cd**	**Cu**	**Pb**	**Zn**
	ppm	Ppm	ppm	ppm
Stipa grass	0.291±0.081	4.194±0.436	0.451±0.049	12.592±1.275
Nafal	0.212±0.068	5.711±0.578	1.323±0.138	17.842±1.802
Ashnan	<0.064	18.292±1.844	1.241±0.125	46.359±4.680
Sheran	<0.064	13.688±1.405	<0.038	61.298±6.176

Table 1 shows the concentration of the four heavy metals at site 1 (near Ramtha city). The results shows that Stipa grass is contaminated with high levels of Cd, Cu, and Pb compared with risk concentrations, while the concentration of Zn is slightly above the risk level. Nafal has a level contamination for all elements. Ashnan is contaminated by high levels of Cu, Pb and Zn while slightly less contamination with Cd. Sheran is contaminated by Cu and Zn and with less levels by Cd and Pb.

Table 2. The concentration of heavy metals at site 2 (near Akader village)

Type	Cd	Cu	Pb	Zn
	ppm	ppm	ppm	ppm
Stipa grass	0.101±0.018	3.240±0.329	<0.038	10.465±1.072
Nafal	0.312±0.123	13.675±1.388	4.804±0.488	113.359±11.491
Ashnan	0.164±0.019	13.371±1.386	0.367±0.040	60.933±6.142
Sheran	<0.064	15.239±1.542	0.956±0.099	81.620±8.256

Table 2 shows the concentration of the four elements in plants at site 2 (near Akhader village). Stipa grass is contaminated with high levels of Cd and Cu and with low level of Pb. On the other hand it is not contaminated with Zn metal. Nafal has a very high level of contamination by all four elements. Ashnan has high level of contamination by Cu, Pb and Zn, and with lesser degree by Cd. Sheran has a very high contamination by Cu and Zn and with lesser degree by Pb and the least is by Cd.

Table 3. The concentration of heavy metals at site 3 (near Jaber village)

Type	Cd	Cu	Pb	Zn
	ppm	ppm	ppm	ppm
Stipa grass	0.075±0.022	2.914±0.301	<0.038	9.761±1.005
Nafal	<0.064	4.604±0.500	<0.038	17.523±1.775
Ashnan	<0.064	4.831±0.503	<0.038	21.005±2.116
Sheran	<0.064	3.993±0.405	<0.038	34.138±3.441

Table 3 shows the concentration of the four elements in plants at site 3 (near Jaber village). Stipa grass exceeds the risk levels of Cd, Cu and Pd, while the concentration of Zn is less than the risk level. Nafal and Ashnan exceeds the risk level of Cd, Cu and Zn and with lesser degree of Pb. Sheran has high concentration level of Cu, Pb and Zn and slightly risk level of Cd.

Table 4. The concentration of heavy metals at site 4 (near Mafraq City)

Type	Cd	Cu	Pb	Zn
	ppm	ppm	ppm	ppm
Stipa grass	0.190±0.045	8.620±0.892	0.164±0.017	35.712±3.612
Nafal	0.171±0.039	4.377±0.468	<0.038	33.476±3.378
Ashnan	0.070±0.007	13.218±1.331	0.073±0.008	53.009±5.336
Sheran	<0.064	16.942±1.718	0.498±0.050	55.389±5.575

Table 4 shows the concentration of the four elements in plants at site 4 (near Mafraq city). Stipa grass is highly contaminated by Cu and Zn and slightly lesser contamination by Cd and Pb. Nafal, Ashnan and Sheran exceed the risk levels for Cu and Zn and with lesser degree with Cd and Pb.

Table 5. The concentration of Cd, Cu, Pb and Zn elements in Stipa grass at the four sites.

Type	Cd	Cu	Pb	Zn
	ppm	ppm	ppm	Ppm
Site 1	0.291±0.081	4.194±0.436	0.451±0.049	12.592±1.275
Site 2	0.101±0.018	3.240±0.329	<0.038	10.465±1.072
Site 3	0.075±0.022	2.914±0.301	<0.038	9.761±1.005
Site 4	0.190±0.045	8.620±0.892	0.164±0.017	35.712±3.612

Tables from 5-8 show the concentration of Cd, Cu, Pb and Zn for each plant in the four sites. Table 5 shows that the concentration of Cd and Pb in Stipa grass at site 1 is more than that at other sites and the concentration of Cu is more than that at sites 2 and 3. The highest concentration of Cd and Pb in Stipa grass is highest at site 1 and least in site 3. On the other hand, Cu and Zn concentrations are highest at site 4 and least at site 3.

Table 6. The concentration of Cd, Cu, Pb and Zn elements in Nafal at the four sites

Type	Cd	Cu	Pb	Zn
	ppm	ppm	ppm	ppm
Site 1	0.212±0.068	5.711±0.578	1.323±0.138	17.842±1.802
Site 2	0.312±0.123	13.675±1.388	4.804±0.488	113.359±11.491
Site 3	<0.064	4.604±0.500	<0.038	17.523±1.775
Site 4	0.171±0.039	4.377±0.468	<0.038	33.476±3.378

From table 6 it can be seen that the concentration of all four heavy metals in Nafal is highest at site 2 and least at site 3 especially the concentration of Cu and Zn.

Table 7. The concentration of Cd, Cu, Pb and Zn elements in Ashnan at the four sites

Type	Cd	Cu	Pb	Zn
	ppm	ppm	ppm	ppm
Site 1	<0.064	18.292±1.844	1.241±0.125	46.359±4.680
Site 2	0.164±0.019	13.371±1.386	0.367±0.040	60.933±6.142
Site 3	<0.064	4.831±0.503	<0.038	21.005±2.116
Site 4	0.070±0.007	13.218±1.331	0.073±0.008	53.009±5.336

Table 7 shows that the concentrations of Cd and Zn in Ashnan are highest at site 2 while the highest concentrations of Cu and Pb are at site 1. A gain the least concentration of all four metals is at site 3.

Table 8. The concentration of Cd, Cu, Pb and Zn elements in Sheran at the four sites

Type	Cd	Cu	Pb	Zn
	ppm	ppm	ppm	ppm
Site 1	<0.064	13.688±1.405	<0.038	61.298±6.176
Site 2	<0.064	15.239±1.542	0.956±0.099	81.620±8.256
Site 3	<0.064	3.993±0.405	<0.038	34.138±3.441
Site 4	<0.064	16.942±1.718	0.498±0.050	55.389±5.575

Table 8 shows that the concentration of Cd in Sheran is the least at all sites. The highest concentration of Pb and Zn is at site 2 while the least is at site 3. The concentration of Cu is maximum at site 4 and minimum at site 1.

Table 9. The concentration of Cd in all four plants at the four sites

Type	Stipa grass	Nafal	Ashnan	Sheran
	ppm	ppm	ppm	ppm
Site 1	0.291±0.081	0.212±0.068	<0.064	<0.064
Site 2	0.101±0.018	0.312±0.123	0.164±0.019	<0.064
Site 3	0.075±0.022	<0.064	<0.064	<0.064
Site 4	0.190±0.045	0.171±0.039	0.070±0.007	<0.064

Tables from 9-12 show the concentration of each heavy element in all four plants at all sites. From table 9 one can see that the least concentration of Cd in all plants exists at site 3. Also Sheran has the least concentration of all plants at all sites. Sites 1, 2 and 4 have plants with considerable concentrations of Cd in plants A and B, while the concentration of Ashnan is high at site 2 only.

Table 10. The concentration of Cu in all four plants at the four sites

Type	Stipa grass	Nafal	Ashnan	Sheran
	ppm	ppm	ppm	ppm
Site 1	4.194±0.436	5.711±0.578	18.292±1.844	13.688±1.405
Site 2	3.240±0.329	13.675±1.388	13.371±1.386	15.239±1.542
Site 3	2.914±0.301	4.604±0.500	4.831±0.503	3.993±0.405
Site 4	8.620±0.892	4.377±0.468	13.218±1.331	16.942±1.718

Table 10 shows that site 3 almost has the least concentration of Cu in all four plants. All plants have higher concentrations of Cu at all other sites.

Table 11. The concentration of Pb in all four plants at the four sites

Type	Stipa grass	Nafal	Ashnan	Sheran
	ppm	ppm	ppm	ppm
Site 1	0.451±0.049	1.323±0.138	1.241±0.125	<0.038
Site 2	<0.038	4.804±0.488	0.367±0.040	0.956±0.099
Site 3	<0.038	<0.038	<0.038	<0.038
Site 4	0.164±0.017	<0.038	0.073±0.008	0.498±0.050

Table 11 shows that the least concentration of Pb in all four plants is again at site 3. On other hand, the concentration at other sites is little bit higher for all plants.

Table 12. The concentration of Zn in all four plants at the four sites

Type	Stipa grass	Nafal	Ashnan	Sheran
	ppm	ppm	ppm	ppm
Site 1	12.592±1.275	17.842±1.802	46.359±4.680	61.298±6.176
Site 2	10.465±1.072	113.359±11.491	60.933±6.142	81.620±8.256
Site 3	9.761±1.005	17.523±1.775	21.005±2.116	34.138±3.441
Site 4	35.712±3.612	33.476±3.378	53.009±5.336	55.389±5.575

The concentration of Zn in all four plants is least at site 3 as can be seen from table 12. While the concentration is almost highest at site 2 followed by site 4 and 1 respectively.

80-90% of Pb emissions into the atmosphere are caused by the combustion of alkyl Pb additives in motor feul. Other sources of Pb pollution are mining and smelting of Pb ores (Ziemacki et al 1989). Cd compounds are used in metal electroplanting, as stabilizers or pigments in plastics, in alkaline batteries and in alloys(Ziemacki et al 1989). Some studies indicated that urban sewage contains substantial amounts of copper (Sciortino and Ravikumar 1999).

Industrial activities such as coal and waste combustion represented zinc contaminants (Greany 2005). The greatest concentrations of Cd, Pb, and Zn are in sewage sledges (Basta et al 2005), followed by phosphate fertilizers (Sumner 2000).

The results show that plants are almost contaminated with metals at all selected sites, with small concentration at site 3. A fraction of this contamination can be due to the heavy traffic transportation on this highway. But the contamination levels are not equal ,which may correspond to other sources. Site 2 has the highest levels of contamination , followed by sites 1 and 4 respectively. The high level of contamination at site 1 is mainly due to the exhausts of the factories at Al-Hassan Bin Talal industrial area which is about 300m away from the sampling site. Site 2 is located about 1km from the main dumpsite of all northern regions of Jordan. Firing the garbage from time to time can contaminate the area with heavy metal compounds as seen in the plant samples. Site 4 is located near the Sewage plant of Mafraq city, which is also may be a source of contamination of plants at that site.

Actually site 3 is an open region that is about 7km apart from the nearest contaminated region in site 2. This may explain the low level of contamination at that site.

4. Conclusion

This study shows that all of the chosen sites, which represent agricultural areas and pastures, are exposed to unevenly contamination sources. The contamination in Site 2 and even in site 3 which is the least contaminated area could be decreases by stopping firing garbage by recycling it artificially and naturally. Studying the contamination of soil and water with heavy metals in these regions especially at sites 1 and 4 is very important to identify all sources of contamination.

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