SEASONAL VARIATIONS IN HEAVY CONCENTRATIONS IN AGRICULTURE SOILS IN TEHERAN-IRAN

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ABSTRACT
Seasonal variations and different concentrations of the heavy metals - Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn - in agricultural soil near the high way, Tehran, Iran were investigated during the two major seasons. Soil Samples were collected during the 2009 and 2010 rainy and dry (summer and winter) seasons were treated and digested using standard wet digestion methods. Heavy metals were determined with Atomic Absorption Spectrophotometer (AAS). Analytical results from agriculture soils in Teheran-Iran indicated that in the winter and summer seasons, at station one manganese, zinc are maximum in concentration and iron, nickel are in minimum concentration. Station 2 has iron and nickel in maximum concentration while chromium is observed to be minimum at station 2. At station 3 copper, leads are observed to be in maximum as compared to other stations. Also, at station 5 chromium is more in concentration while manganese is minimum.

Key words: Heavy metals, agricultural soils, pollution, Tehran.

INTRODUCTION
Heavy metal concentration in agricultural soils can affect human beings directly, through soil ingestion or through the food web by ingestion of crops and animals. Indirectly it causes severe damage of environmental health. Atmospheric deposition of heavy metal, urban–industrial activities and agricultural practices by using agrochemical products are the main anthropic sources of heavy metals in agricultural soils. An increase in heavy metal deposition in agricultural soils and crops are observed due to transport of heavy vehicles near the agricultural farm. Awofolu (2004) recorded impact of automobile exhaust on levels of lead in a commercial food from bus terminals. Vegetables constitute essential components of the diet. They are contributing protein, vitamins, iron, calcium and other nutrients which are essential for human health. Contamination of vegetables with heavy metal may be due to irrigation with contaminated water, addition of fertilizers, industrial emissions, transportation, etc. These food plants contain both essential and toxic metals over a wide range of concentration. Consumption of crops by human and fodder for animals are major factors of damaging human health. In India heavy metal contamination study of soil and vegetables of Varansi has been carried out by Sharma (2007). A survey along two national highways near Lucknow was carried out. The pattern of lead deposition as reflected by soil Pb burdens, showed that decrease in concentration with increasing distance from the road margins. At both the sites lead concentration was above back ground concentration at the soil depth of 15 cm. Some plants contained high concentration of Pb over their respective controls, with more accumulation in the underground portions of the plants. The cattle grazed near the roadside pastures, naturally milk sample contained lead at an elevated concentration (Singh et al. 1997).

Heavy metals studies have been conducted in soils with differing levels of anthropogenic influences such as in highly populated and industrialized cities. Karbassi (2003) reported heavy metals such as Cu, Cr, Cd, Ni, and Pb are potential soil and water pollutants. Hamzeh (2006) carried out analytical study of heavy metals of environmental effluents at Kerman, Iran. Heavy metal studies are necessary to evaluate both soil/sediment and groundwater contamination. The problem of environmental pollution due to toxic metals has begun to cause concern now in most major metropolitan cities. The toxic heavy metals entering the ecosystem may lead to geo-accumulation, bio-accumulation and bio-magnifications. Heavy metals like Fe, Cu, Zn, Ni and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in bio-systems through contaminated water, soil and air. Oluyemi et al. (2008) carried out seasonal variation in heavy metal concentrations in soil and some selected crops at a landfill in Nigeria. The seasonal variations in concentrations of the heavy metals - As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn - in soil and crops from a farm near the refuse dump site of Obafemi Awolowo University, Ile-Ife, Nigeria were investigated during the two major seasons of Nigeria. This was done to assess the pollution status.
of the farm and hence the safety levels of the crops produced. Present attempt is made to know effect of seasonal variation on soils of Teheran-Iran due to heavy metal pollution.

MATERIALS AND METHODS

Area under study:

Tehran Province is one of the 31 provinces of Iran. It covers on area of 18,909 square kilometers and is located to the north of the central plateau of Iran. Tehran Province borders Mazandaran Province in the north, Qom Province in the south, Semnan Province in the east, and Qazvin Province in the west. The metropolis of Tehran is the capital city of the province and of Iran. As of June 2005[update], this province includes 13 townships, 43 municipalities, and 1358 villages. Tehran province is the richest province of Iran as it contributes approximately 29% of the country's GDP. Furthermore, it houses approximately 18% of the country's population. Tehran Province is the most industrialized province in Iran; 86.5% of its population resides in urban areas and 13.5% of its population resides in rural areas. The province gained importance when Tehran was claimed the capital by the Qajar dynasty in 1778. Today, Tehran, with a population of more than 7 million, is ranked amongst the 20 most populous metropolitan cities of the world.

Tehran’s air quality is impacted by the stationary and mobile sources as well as its location and topography. It is estimated that about 30% of Iran’s industrial establishments are located around Tehran (BBC Persian.com, January 2, 2005). Of these establishments, metal and chemical factories are located mostly up wind to the west of the city, a refinery to the south, and small factories throughout the city. Stationary sources (industries and residential/commercial services) accounted for approximately 29% of the air pollution while approximately 71% of Tehran’s air pollution was related to mobile sources (Hastaie 2000b). Tehran had about 1.3 million motor vehicles in 1996. Approximately, 700,000 of the total were privately-owned cars. In addition, there were 350,000 motorcycles in the city in 1996 (Tehran Comprehensive Transportation and Traffic Studies Company 1996). By 2000, the number had reached to about 2 million vehicles operating in an extremely congested road network (Hamshahri 2000), with an average vehicle speeds below 18 km/h (Hastaie 2000a). The most recent data indicates that approximately 2.5 million of Iran’s 7.5 million vehicles are located in Tehran (33%) while the city has about 10% of Iran’s total population of 69.51 million (Hamshahri, August 7, 2006, United Nations Department of Economic and Social Affairs/Population Division 2005). Iran’s auto industry has boomed in recent years to become one of the biggest sectors outside of oil, employing 150,000 and accounting for about 4% of GDP. Iran boasts the largest car industry in the Middle East and Central Asia. Since 2000, Iran’s auto manufacturers have increased their annual production from approximately 300,000 to about 1 million vehicles (BBC Persian.com, December 14, 2005). According to The Economist (2003), ‘Every day 1200 vehicles and 600 motorcycles join the existing fleet in Tehran, clogging the streets with traffic and choking everyone with fumes. The cost of traffic congestion in the capital is put at 2 billion hours of time wasted each year’. One major characteristic of the auto fleet that has had a significant impact on Tehran’s air quality is the age factor. It is reported that Tehran’s autos were in average 17 years old (The Economist, 2003). It is estimated that about 1.5 million old vehicles (20 years and older) are operating across the country. Of the total, about 600,000 are in Tehran (Hamshahri 2005). The high number of old and polluting vehicles is a major cause of the air pollution in Tehran. The problem of air pollution is compounded by the topographical and meteorological factors. Mountains surround Tehran to the north and east with flat terrain to the south and west. The mountains block the movement of Tehran’s air and thus hinder the dispersion of air pollutants. The local winds are often not strong enough to circulate the air. In addition, the major winds blow from the west, south, and southeast, where most of the industries are located. Rather than cleaning the air, they can pollute the air further (Madanipour 1998). Tehran’s topography and its surrounding mountain systems intensify the temperature (atmospheric) inversion in fall and winter seasons. Each year, Tehran faces the problem of temperature inversion for about 250 days. The temperature inversions push dense clouds of stagnant smog down onto the city. Air pollution mitigation master plan and strategies in the past 10 years, the Government of Iran and Tehran Municipality have actively participated in an effort for the reduction of local and global air pollution. Present study has been carried out around Tehran in six sites (Map).

Data collection and analysis:

36 Soil samples (six stations and every station three samples 5m, 10m, 15m and opposite site) were collected at surface level (0–10 cm in depth) were collected from various locations to cover industrial, commercial and residential areas. The collected soil samples were air-dried and sieved into coarse and fine fractions. Well-mixed samples of 2 g each were taken in 250 mL glass beakers and digested with 8 mL of aqua regia on a sand bath for 2 hours. After evaporation to near dryness, the
samples were dissolved with 10 mL of 2% nitric acid, filtered and then diluted to 50 mL with distilled water. Heavy metal concentrations of each fraction were analyzed by Atomic Absorption Spectrophotometry. Quality assurance was guaranteed through double determinations and use of blanks for correction of background and other sources of error. EC of the soil samples were determined from saturation extract by conductivity meter. Measurement of pH of the soil samples was done with help of a glass electrode pH meter.

**Table: Six sites were selected around Tehran for data collection.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Stations</th>
<th>Name of station</th>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td>Saidi highway (shahid beheshty complex)</td>
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<tr>
<td>2</td>
<td></td>
<td>Saidi highway (shah Tareeh)</td>
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<td>3</td>
<td></td>
<td>Tehran-Qom highway (Turouz abad)</td>
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<td>4</td>
<td></td>
<td>Tehran-Qom highway (Jalil Abad)</td>
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<tr>
<td>5</td>
<td></td>
<td>Tehran-Varamin highway (near Amin Abad road)</td>
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<tr>
<td>6</td>
<td></td>
<td>Tehran-Varamin highway (Firooz Abad)</td>
</tr>
</tbody>
</table>

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RESULTS AND DISCUSSION

The heavy metal analysis of various soil samples collected from six different locations in and around Tehran, Iran was reported.

Zinc: The amount of zinc in the agricultural soils around Tehran in summer season ranged from 0.76 to 2.12 μg/g with the mean value of 1.43 μg/g in summer season (Figure 1). Maximum zinc concentration is observed at station three, 2.12 μg/g Tehran-Qom highway (Turouz abad) whereas minimum zinc concentration is observed at station four, 0.76 μg/g Tehran-Qom highway (Jalil Abad).
The amount of zinc in the agricultural soils in winter season around Tehran ranged from 5.52 to 15.26 μg/g with the mean value of 8.01 μg/g (Figure 2). Maximum zinc concentration is observed at station one, 15.26 μg/g Saidi high way (shahid beheshty complex) whereas minimum zinc concentration is observed at station six, 5.52 μg/g Tehran high way (Firooz Abad).

Normal concentrations of zinc in soil range from 1 to 900 μg/g (Alloway 1995). So in this study, all sampled were in the normal range and none exceeded.

**Copper:** The copper content in the agricultural soils around Tehran in summer, ranged from 3.60 to 21.60 μg/g with the mean value of 9.90 μg/g (Figure 3). Maximum Cu concentration is observed at station...
six, 21.60 μg/g Tehran-Varamin high way (Firooz Abad) while minimum Cu concentration is observed at station four 3.60 μg/g Tehran-Qom high way (Jalil Abad). The copper content in the agricultural soils in winter around Tehran ranged from 3.90 to 14.45 μg/g with the mean value of 8.27 μg/g (Figure 4). Maximum Cu concentration is observed at station three 14.45 μg/g Tehran-Qom high way (Turouz abad)) while minimum Cu concentration is observed at station four 3.90 μg/g Tehran-Qom high way (Jalil Abad). The normal Cu content of agricultural soils is 5 to 50 μg/g. Concentrations below 8 μg/g could indicate a deficiency for some crops as Cu is an essential micronutrient (McBride, 1994; Kabata-Pendias and Pendias (2001). In this study, all sampled were in the normal range and none exceeded.

**Iron and manganese**

In general, the soil Fe and Mn concentrations are not reported in studies focusing on soil heavy metal content because they are not contaminant elements. Both metals are important in plant nutrition as they are essential crop micronutrients. These elements can be in insoluble forms in calcareous soils causing deficiencies (e.g. ferric chlorosis). In spite of elevated soil content, total Fe or Mn are not a good indicator of their plant availability. For example, Fe is mainly present in precipitated forms such as oxides and hydroxides in the soils. Therefore, Fe deficiency does not seem to be due to an insufficient in soils. The iron content in the agricultural soils around Tehran in summer ranged from 2 to 21.60 μg/g with the mean value of 10.50 μg/g (Figure 5). Maximum Fe is observed at station two 21.60 μg/gsaidi high way (shah Tareeh) and minimum Fe is observed at station three 2.00 μg/g, Tehran-Qom high way (Turouz abad).

**Fig. 13:** Concentration of Pb in different stations in summer season Tehran, Iran (μg/g)

**Fig. 14:** Concentration of Pb in different stations in winter season (μg/g)

**Fig. 15:** Concentration of Cd in different stations in summer Tehran, Iran (μg/g)

**Fig. 16:** Concentration of Cd in different stations in winter (μg/g)
The Iron content in the agricultural soils around Tehran in winter ranged from 1 to 18 μg/g with the mean value of 6.69 μg/g (Figure 6). Maximum Fe is observed at station two 18.00 μg/g Saidi high way (shah Tareeh) and minimum Fe is observed at station three, 1.00 μg/g Tehran-Qom high way Turouz abad). Manganese concentration in summer is ranged between 39.30 to 66.90 μg/g with the mean value of 54.05 μg/g (Figure 7). Maximum Mn concentration is observed at station five, 66.90 μg/g (Tehran-Varamin high way (near Amin Abad road) and minimum concentration is observed at station four 39.30 μg/g Tehran-Qom high way (Jalil Abad).

Manganese concentration in winter is ranged between 10.30 to 56.30 μg/g, with the mean value of 23.13 μg/g (Figure 8). Maximum Mn concentration is observed at station one, 56.30 μg/g (Saidi high way (shahid beheshty complex) and minimum concentration is observed at station five, 10.30 μg/g (Tehran-Varamin high way (near Amin Abad road).

Chromium: The concentration of Chromium in summer to the agricultural soils around Tehran ranged from 0.24 to 0.70 μg/g with the mean value of 0.52 μg/g (Figure 9). Maximum Cr is observed at station four, 0.70 μg/g Tehran-Qom high way (Jalil Abad), and minimum concentration is observed at station three, Tehran-Qom high way(Turouz abad).

The concentration of Chromium in the agricultural soils around Tehran in winter is ranged from 0.234 to 1.577 μg/g with the mean value of 0.58 μg/g (Figure 10). Maximum Cr is observed at station five, 1.577 μg/g Tehran-Varamin high way(near Amin Abad road) and minimum concentration is observed at station two, 0.24 μg/g Saidi high way(shahid Tareeh). Maximum permissible agricultural soil concentration for chromium is 100 in some European countries (Mico and Peris 2006). So in this research all sampled were in the normal range.

Nickel: The Nickel content in the agricultural soils around Tehran in summer is ranged from 0.23 to 0.52 μg/g with the mean value of 0.36 μg/g (Figure 11). Maximum Ni concentration is observed at station four, 0.02 μg/g Tehran-Qom high way (Jalil Abad), and minimum concentration is observed at station two, 0.35 μg/g Saidi high way(shah Tareeh).

The Nickel content in the agricultural soils around Tehran is ranged from 0.02 to 0.35 μg/g with the mean value of 0.66 μg/g in winter. (Figure 12) Maximum Ni concentration is observed at station two, 0.02 μg/g Saidi high way(shah Tareeh) and minimum concentration is observed at station one, 0.35 μg/g (Saidi high way (shahid beheshty complex).

The normal soil Ni content varies from 1 to 100 μg/g (Pendias and Pendias, 2001). In this study all sampled were in this range.

Lead: In the last decades, much attention has been directed towards lead in the roadside environments as a result of its widespread use as an anti-knocking agent in gasoline (Davies & Holmes, 1972; Wheeler & Rolf, 1979; Hafen & Brinkmann, 1996; Turer & Maynard, 2003). In the recent years, the lead content in gasoline was markedly decreased in the world. This decrease has reduced the addition of lead to the environment by motor vehicles. However, the previously deposited lead remains a major contaminant of the roadside environments. Although the lead content in gasoline is minimized these days, the increased traffic has caused an increase in the lead emission in the roadside environment.

In the present study, the lead content of the agricultural soil in summer ranged from 0.18 to 0.43 μg/g with the mean value of 0.28 μg/g (Figure 13). Maximum Pb concentration is observed at station three, 0.43 μg/g Tehran-Qom high way (Turouz abad) and minimum concentration is observed at station four, 0.18 μg/g Tehran-Qom high way (Jalil Abad).

The lead content of the agricultural soil in winter ranged from 0.18 to 1 μg/g with the mean value of 0.59 μg/g (figure14). Maximum Pb concentration is observed at station three, 1.00 μg/g Tehran-Qom high way (Turouz abad) and minimum concentration is observed at station four, 0.18 μg/g Tehran-Qom high way (Jalil Abad).

Cadmium concentration of the agricultural soil is ranged between from 0.00 to 0.004 μg/g with the mean value of 0.002 μg/g (Figure 15) in summer season. Cadmium concentration of the agricultural soil ranged between from 0.001 to 0.004 μg/g with the mean value of 0.002 μg/g in winter season. (Fige 16)

DISCUSSION AND CONCLUSION

The study reveals that, Seasonal variation in heavy metals concentration is observed at each station. Zinc concentration is 2.212 mg/g and 15.26 mg/g maximum at station 3 and 1 in summer and winter respectively. Concentration of iron is maximum 21.60 in station 2 in summer and 18.00 mg/g in station 2 at summer and winter season. Nickel are in maximum concentration at station 4 and 2 i.e. 0.02 in summer and winter. Maximum concentration of chromium is observed at station 4 and 2 0.70 and 1.57 in summer and winter. Copper concentration is maximum in station 6 and 3, 21.60 mg/g and 14.45 mg/g in summer and winter season. Lead concentration is maximum at station 30.43 mg/g and 1.00 mg/g in both the season. Concentration of Manganese observed to be in maximum in station 5 and one ,66.90 and 56.30 in summer and winter respectively. As compared to minimum concentration at different stations are Zinc.
in 4 (0.76 mg/g) and 6 (5.52 mg/g) in summer and winter; Copper at station 4, 3.60 mg/g and 3.90 mg/g in summer and winter. Fe station 3, 2.00 mg/g and 1.00 mg/g in both season respectively. Manganese concentration at station 4 and 5 39.30 mg/g and 10.30 mg/g in summer and winter season respectively. Chromium is minimum in station 3 and 2, 0.24 mg/g in summer 0.51 mg/g in winter season. Nickel is minimum at station 2 and one in same concentration 0.35 mg/g. Similarly lead is minimum 0.18 mg/g in station 4 in summer and winter. This indicate that seasonal variation of heavy metal concentration is one of the major factor of pollution. At some stations it was observed that no change in heavy metal concentration due to season variation. It is important to understand metal toxicity of road side soil and vegetation in different seasons. The effect of pollution can be minimize by plantation of suitable hyper-accumulator plants to rehabilitate contaminated areas and regulate metal emissions effectively

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