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HEAVY METAL ACCUMULATION IN SOILS AROUND A SALT LAKE IN TURKEY

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Abstract

The heavy metal (Pb, Cr, Cu, Mn, Ni, Zn and Cd) accumulation around soils of Salt Lake in Turkey were evaluated, accounting for major sources including atmospheric deposition, sewage systems, livestock manures, fertilizers, traffic and industrial by-product wastes. The heavy metal concentrations were determined by using Varian model Inductively Coupled Plasma and statistically evaluated with SPSS 11.5 statistical program. The heavy metal concentrations were investigated monthly except winter months. The lowest and the highest accumulation levels were observed in April and in August, respectively. The soils were also evaluated according to zonation around the lake and the relations between the four selected stations. There is a correlation between the heavy metals and their sources. There should be some precautions taken against the heavy metal pollution around Salt Lake because of the ecological, agricultural and economical importance of the area.

Introduction

Soil contamination by heavy metals such as Pb, Cr, Cu, Mn, Ni, Zn and Cd is a matter of great concern. Unlike organic contaminants that loose toxicity by the time with biodegradation, heavy metals can not be degraded, their concentration can be increased by bioaccumulation and they have toxic effects at low concentrations (Aksoy, 2008; Clark, 1992; Davey *et al*., 1973; Hussain *et al*., 2008). Although low quantities of some heavy metals, such as copper and zinc, are essential for many organisms, they are potentially toxic and accumulate in soil over long period of time and this result in soil pollution (Ahmad *et al*., 2008). The main sources of heavy metals are fertilizers from agricultural areas, livestock manure, air pollution and emissions from vehicles. The metals accumulate in the salt marshes from polluted air *via* rain, near roads *via* splash water or by irrigation with waste water and fertilization with waste compost (Blume & Brümmer, 1991; Blake & Goulding, 2002; Patel *et al*., 2001; Setyorini *et al*., 2002). Over a period of time all these sources enrich heavy metals in soil. Excessive heavy metal contents changes the soil quality which affects the normal use of soil or endangering public health and living environment. Pollution of agricultural soils by heavy metals may lead to reduced yields and elevated levels of these elements in agricultural products and thus provide their entrance into food chain. Soil constituents may immobilize heavy metals, so prevent or reduce the detrimental effects on soil organisms, crops and ground water quality (Blume & Brümmer, 1991; Ahmad *et al*., 2007).

Salt marshes act as a sink for organic pollutants and heavy metals (Adam, 1999). Collectively salt marshes can be seen to be acting as dynamic filters for various ecologically important materials (Vernberg, 1993). In salt marshes under anaerobic conditions insoluble sulphates and clay minerals bind heavy metals through cation exchange. Also the high pH value immobilizes the heavy metals (Kimberly & William, 1999).

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Salt marshes have important aesthetic, cultural, economic, recreational, scientific, conservational and ecological values (Williams, 1993; 2002). They provide nesting and breeding sites especially for migrating birds. Salt Lake which was declared as a Specially Protected Area and one of the hotspots of Turkey, is rich in halophytic endemic plant species and also on the route of immigrant birds and provides suitable areas for them. This area not only has an ecological importance but also has an economical importance. It is also one of the important salt resources of Turkey. Around Salt Lake agriculture and animal breeding is very important. Main crop plants of the region are *Beta vulgaris* ssp. *altissima, Hordeum vulgare* and *Triticum sativum*. For conservation, management and recovery of the area there is a requirement for knowledge of soil chemistry. There is a plant zonation according to the salinity around Salt Lake. Plant species composition changes and plant biodiversity increases with decreasing salinity.

In this study it was aimed to investigate the heavy metal concentrations of soils around Salt Lake. The heavy metal accumulation was investigated monthly and evaluated according to the plant zones and the stations chosen from different regions of the lake.

Material and Methods

Salt Lake is in the Central Anatolian region of Turkey (Fig. 1). The study area is under the influence of semi-arid cold Mediterranean climate. Precipitations occur in cold season. There is a severe drought starting at June and continuing till the end of November. The dominant wind direction which carries the air pollution is as follows; in Kulu from NNW and NNE, in Cihanbeyli NNW and WSW, in Sereflikochisar N and in Aksaray ENE.

Soil samples were taken from 4 different stations (Kulu, Cihanbeyli, Aksaray and Sereflikochisar) in 9 months (August, September, October, November 2003 and March, April, June, July 2004), and could not taken from December to March because of the snow cover and climatic conditions. Coordinates were determined by Global Positioning System (GPS). Collected soil samples were air dried for 4 days until they reach constant weight. Dried aliquots were ground using a mortar and pestle and sieved through 2 mm sieve. Then, the samples stored in polyethylene bags in a desiccator with calcium chloride to avoid contamination throughout the analyses. Acid washed glassware, analytical grade reagents and double distilled water were used throughout the experiments.

All standards were prepared from reagent grade chemicals (Merck, Darmstadt, Germany). Triplicate sub samples of approximately 1 g of well homogenized sediment samples were accurately weighed on an analytical balance and then transferred into glass digestion tubes. Aqua-regia ($1HNO_3$:3 HCl) were used to leach the samples (Demirezen & Aksoy, 2004). The extracts were diluted to a final volume of 50 ml using double distilled water. The concentrations of Pb, Cr, Cu, Ni, Zn and Cd were determined in the supernatant using a Varian model Inductively Coupled Plasma (ICP-OES).

SPSS 11.5 statistical program was used to calculate standard deviations and means. In this study, α was chosen to be 0.05. Results of testing were considered significant if calculated p-values were ≤ 0.05. For the comparison of the means ANOVA test and Post Hoc Duncan test were used.

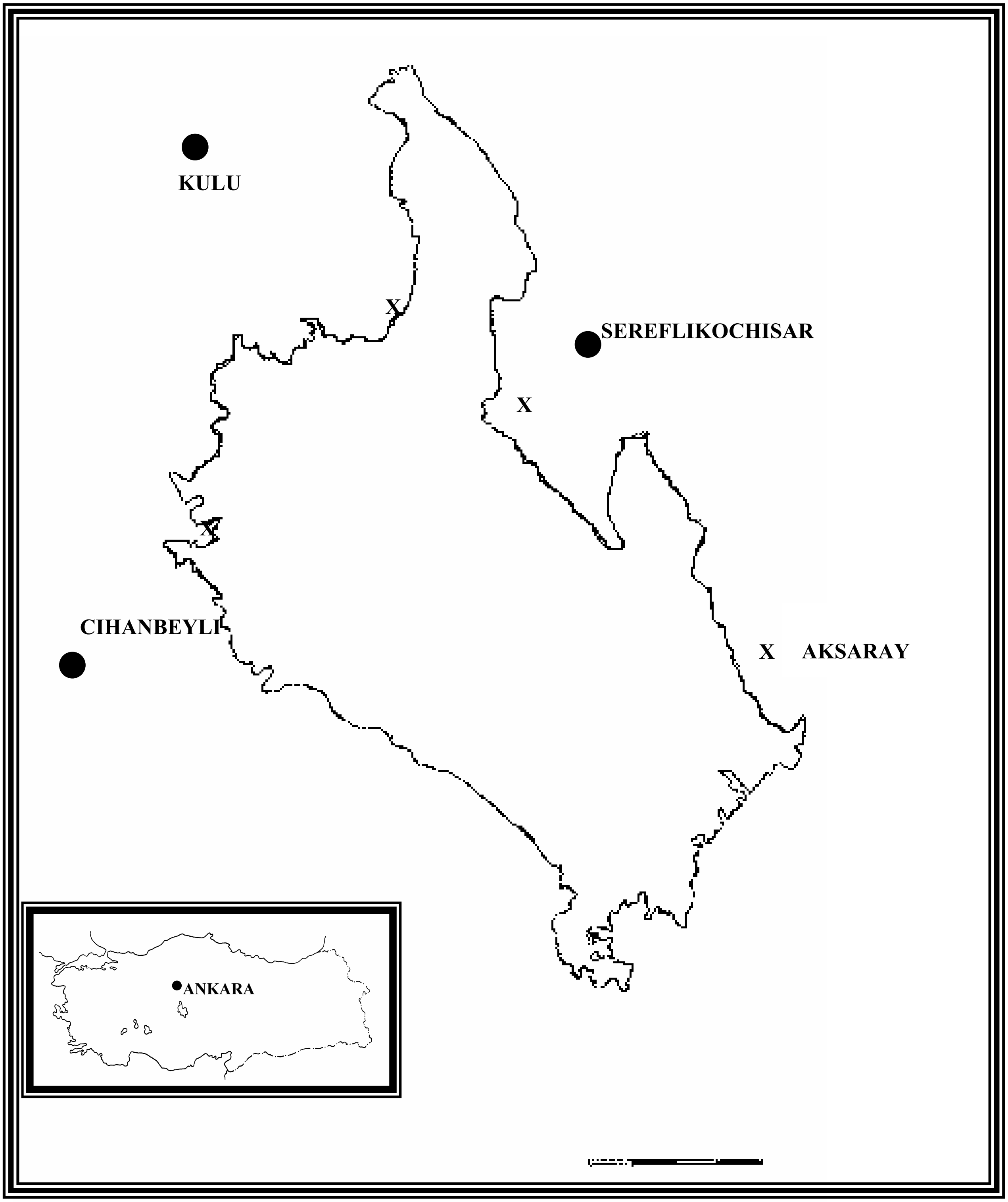

Fig. 1. Map of the study area.

Results and Discussion

In soil samples taken from 4 different stations of Salt Lake Pb, Zn, Cr, Cu, Ni and Cd were investigated and the results were evaluated statistically. Pb is present in all soils, rivers, lakes and sea water (Lone *et al.*, 2006). Main source of Pb is the alkyl derivatives in petroleum (Singh *et al.*, 1997). Also metal manufacturing, sewages, paints containing Pb, phosphateous fertilizers, pesticides and ashes are the other sources. Pb is in the form of halide salts in automobile exhaust, and is unstable and easily converted to oxides, carbonates and sulphates (Lone *et al*., 2006). In the developing world although there are some regulatory measures to control the Pb emissions, it is still one of the major global environmental problem in many countries (Yang *et al*., 2000). In this study, it was found that Pb concentration was lowest in Kulu (Table 1). Agriculture and animal breeding are the major activities around Kulu, and there is not any main Pb source. Pb pollution was highest at Cihanbeyli station which is located close to a heavy traffic, residential area and also animal breeding activities. Sewages and traffic was thought to be the main sources of Pb pollution. The pollution level in Sereflikochisar and Aksaray is in between the other stations. Lead is generally penetrated to the soil by aerial deposition along the road sides (Aksoy, 2008). The cause of Pb accumulation in Aksaray was thought to be the traffic emissions and domestic wastes and sewages in Sereflikochisar.

There are so many sources of Zn like fossil fuels, metal manufacturing and fertilization (Markert, 1993). Zn is more reactive and mobile than Cu and Pb and moves through the soil profile, accumulate at the active zone of soil (Claridge, 1995). According to the Table 1 it can be said that the Zn concentrations of each station are close to each other. The main sources of these concentrations are caused mainly by fertilization activities.

The main sources of Cr pollution are the plastic wastes, septic wastes and sewages. According to the Barnhart (1997) 40% of Cr pollution is caused by tanning of leather. Chromium is a naturally found in rocks, animals, plants, soil, and in volcanic dust and gases. It is usually occurs in two forms; chromium (III) and chromium (VI). The natural and essential one is the Chromium (III), whereas chromium (VI) is generally by-product of industrial activities and considered to be more mobile and toxic (Paiva *et al*., 2009). The mobilization, subsequent uptake and the toxicity of the Cr depend on the metal speciation, which determines the impact of it on the physiology of plants (Shanker *et al*., 2005). The highest Cr pollution level was measured at Sereflikochisar. The lowest value was measured at Cihanbeyli. The values at Kulu and Aksaray were close to each other (Table 1).

Cu enters into the ecosystem *via* so many sources like house device industry, wood and metal manufacturing, pesticide usage, animal manures and septic tanks. The highest Cu pollution was observed at Aksaray where the cause can be the domestic wastes, sewages and artificial fertilizers usage. Also one of the reason of this high value can be the presence of high voltage lines close to the station which is also known as a Cu source (Markert, 1993). The Cu levels of other three stations were close to each other and common characteristics of these stations that can cause Cu pollution are agriculture and animal breeding.

The most important sources of Cd are metal industry, plastics and sewages (Allen, 1989) and some special phosphate fertilizers that contain Cd. Because of its high toxicity and great solubility in water Cd is a dangerous pollutant (Liu *et al*., 2006). It is very toxic to animals and plants and plants' exposure to Cd causes reductions in photosynthesis, water and nutrient uptake (Sanità di Toppi & Gabbrielli, 1999). The Cd results similar to the results of Cu. The highest value was measured at Aksaray station. The main source of Cd at this station was thought to be sewages and phosphate fertilizers used in agricultural areas. But it was known that the influence of phosphate fertilizers is low and only evident after a long term period (Kobza, 2005). There wasn't any important difference between the other three stations and there was low Cd accumulation at these stations.

Table 1. Annual mean heavy metal concentrations (±SD) in each station (μg g^{-1} dry weight).

Stations	Pb	Zn	Cr	Cu	Ni	Cd
Kulu	8.07±2.83 ^{a}	36.13±13.99 ^{a}	49.32±20.62 ^{ab}	21.06±8.57 ^{a}	66.1±30.96 ^{a}	0.18±0.1 ^{a}
Cihanbeyli	11.85±3.4 ^{c}	51.45±22.27 ^{b}	40.75±15.26 ^{a}	26.93±7.2 ^{a}	62.83±24.46 ^{a}	0.19±0.07 ^{a}
Sereflikochisar	10.35±3.15 ^{b}	40.59±17.97 ^{ab}	63.14±40.9 ^{b}	24.63±13.27 ^{a}	102.34±69.07 ^{b}	0.21±0.14 ^{a}
Aksaray	9.09±1.61 ^{ab}	52.45±19.64 ^{b}	49.15±19.72 ^{ab}	40.09±9.55 ^{b}	68.74±30.55 ^{a}	0.76±0.1 ^{b}

-Different letters in same column indicate significant differences at p<0.05 (ANOVA)

- SD: Standard deviation

Table 2. Annual mean heavy metal concentrations (±SD) in each plant zones (μg g^{-1} dry weight).

Zone	Pb	Zn	Cr	Cu	Ni	Cd
1	9.35±3.17 ^{a}	41.92±17.63 ^{a}	47.71±27.42 ^{a}	25.57±11.81 ^{a}	71.1±44.99 ^{a}	0.3±0.7 ^{a}
2	9.74±3.04 ^{ab}	47.84±23.02 ^{a}	51.34±23.67 ^{a}	28.56±13.96 ^{ab}	75.82±42.69 ^{a}	0.3±0.6 ^{a}
3	10.48±3.1 ^{b}	45.48±17.38 ^{a}	52.83±29.32 ^{a}	30.09±9.62 ^{a}	78.44±47 ^{a}	0.4±0.7 ^{a}

-Different letters in same column indicate significant differences at p<0.05 (ANOVA)

-SD: Standard deviation

The highest Ni concentration was measured at Sereflikochisar. Main sources of Ni are automobile tyres, at this station, old automobile tyres used to build garden fences. There was not any important difference between the other three stations.

When the zones around Salt Lake were evaluated (Table 2), it was found that the Pb and Cu concentrations was decreased toward the lake. The main source of Pb is air pollution caused by combustion of oil, gasoline and coal. Also the wind at the study area blows from lake and carry dust with heavy metals coming from the sediment of lake. The increase in Pb and Cu can be explained by the heavy traffic and wind direction. For Zn, Cr, Ni and Cd concentrations there wasn't any statistically important difference between the stations. High level of pollution caused by agriculture at outer zone could be explained by the presence of agricultural areas that are close to or at the outer zone.

The fluctuation of heavy metal concentrations in soil for 9 months were also statistically evaluated (Table 3). The lowest Pb, Zn, Cr and Ni concentrations were measured in April. This can be explained by the snow cover preventing penetration of pollutants to soil from December to March. Heavy metals and minerals that become mobile washed into deeper levels of soil and in summer with increasing temperature through the evaporation heavy metals and minerals turns back to upper layers. For this reason, heavy metal concentrations in soil increase in summer. Cu concentration was lowest in November this can be the result of precipitation which increase at the beginning of this month. Cd was lowest in September. The highest level of heavy metals was observed in summer when the evaporation is high. The highest value for Pb, Cr, Ni and Cd was measured in August and for Cu and Zn in June.

Significant and positive correlations determined between all the heavy metals other than the relations between Cd and Pb, Cr, Ni (Table 4). This means that the sources of these pollutants are common. The highest correlation was observed between Pb and Zn and Ni and Cr. The lowest correlation was observed between Cd and the others.

Table 3. Monthly changes in heavy metal concentrations (µg g^{-1} dry weight), together with standard deviations (SD).

Month	Pb	Zn	Cr	Cu	Ni	Cd
August	11.68±3,09 ^{b}	53.45±10.38 ^{cd}	76.58±35.2 ^{d}	28.78±7.67 ^{ab}	115.87±59.17 ^{d}	1.1±1.65 ^{b}
September	11.31±2.37 ^{b}	49.63±13.36 ^{bc}	61.36±15.92 ^{bc}	27.69±10.07 ^{ab}	91.98±26.51 ^{c}	0.16±0.05 ^{a}
October	9.79±2.27 ^{b}	42.56±9.43 ^{b}	52.03±10.12 ^{b}	25.69±7.64 ^{ab}	69.61±14.15 ^{b}	0.18±0.05 ^{a}
November	10.49±3.8 ^{b}	41.95±26.13 ^{b}	29.6±7.43 ^{a}	22.6±10.6 ^{a}	42.1±11.53 ^{a}	0.22±0.12 ^{a}
March	7.99±1.18 ^{a}	30.61±6.59 ^{a}	29.32±6.88 ^{a}	26.62±6.5 ^{ab}	41.14±11.17 ^{a}	0.23±0.26 ^{a}
April	7±0.9 ^{a}	24.43±5.75 ^{a}	26.75±7.02 ^{a}	25.02±9.03 ^{ab}	38.03±9.52 ^{a}	0.2±0.3 ^{a}
May	10.45±3.69 ^{b}	57.12±22.59 ^{cd}	63.35±30.54 ^{bc}	32.32±15.32 ^{bc}	94.89±52.13 ^{cd}	0.21±0.09 ^{a}
June	10.09±3.35 ^{b}	62.3±17.73 ^{d}	67.25±21.74 ^{cd}	36.4±19.76 ^{c}	109.96±41.18 ^{cd}	0.34±0.12 ^{a}

-Different letters in same column indicate significant differences at $p<0.05$ (ANOVA)

Table 4. Correlations between heavy metals in soil samples.

	Pb	Zn	Cr	Cu	Ni	Cd
Pb	1					
Zn	0.731(**)	1				
Cr	0.494(**)	0.619(**)	1			
Cu	0.408(**)	0.668(**)	0.507(**)	1		
Ni	0.507(**)	0.600(**)	0.979(**)	0.508(**)	1	
Cd	-0.005	0.163(**)	0.063	0.121(*)	0.044	1

**Correlation is significant at the 0.01 level; *Correlation is significant at the 0.05 level

Conclusions

Around Salt Lake, the heavy metal pollution increases as a result of human activities which also cause changes in the chemistry of the soil. The main causes of pollution are sewages, domestic waters, air pollution and fertilizers. The pollution level decreases after winter months and then increases in summer. The alkaline soils at the study area provide a kind of self-protection by immobilizing heavy metals at high pH. Some precautions should be taken because of its ecological, economical and agricultural importance.

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