Investigation on Heavy Metal Pollution ın Uludag Fir Forests (A*bies nordmanniana* subsp. *bornmülleriana* MATTF) in the Bartın Region

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Abstract

In this study carried out in pure Uludağ fir forests of Bartın-Ardıç district the change of amount of heavy metals in both soil and needles of Uludag fir depending on altitude was investigated. For this reason, experimental areas were established in three different altitude levels (1,000 m, 1,100 m and 1,200 m) and changes of heavy metals were determined in the soil and Uludag fir needles. According to the results obtained from this research, soil and plant contamination by heavy metals is increasing nowadays while the heavy metal (Pb, Zn, Ni, Cu, Cd, Mn, Cr and Fe) concentrations decreased with the increase in altitude. The highest levels of Cd, Cr and Fe were found in the composite soil and needle of Uludag fir adjacent to 1,000 m and other altitude levels. However, there are significant differences at the $P<0.01$ level according to the results of ANOVA in the amount of heavy metals in both soil and needle of Uludag fir depending on the altitude levels. The Duncan test was also applied and three different groups were found (exception of Cd); the changes of the amount of heavy metals in soil and needle of Uludag fir depends on the altitude level at the $P<0.01$ significance level. In this context, the area should be carefully monitored in order to detect changes in the long-term risk due to the presence of high concentrations of trace elements in soils. Toxicological tests and risk assessment will also be carried out with newly polluted soils and trees (Uludag fir) from this site to evaluate the actual environmental risk of trace elements and their transfer to the food chain. The grape plant had behaved as a metal indicator for Pb, Mn, Zn, Fe, Cu, Cr and Cd, indicating that it can be used for testing changes in metal availability in soils. The concentrations of metals in both plant species exceeded the limits established for humans and grazing animals impling a health risk linked with the spread of pollution from mining sites to Uludag fir forests in the Ardıç district.

Key words: Uludag fir, heavy metal, altitude range, soil, needle

Introduction

Heavy metal contamination in soil is a major concern because of their toxicity and threat to human life and the environment. Heavy metals and other pollutants such as polycyclic aromatic hydrocarbons are major components of petroleum hydrocarbons including bitumen. Toxic heavy metals entering the ecosystem may lead to geo-accumulation, bio-accumulation and bio-magnifications. They get accumulated in soils and plants in time and could have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange and nutrient absorption) determining the reductions in plant growth, dry matter accumulation and yield. Heavy metals get into plants via adsorption which refers to binding of materials onto the surface or absorption which implies penetration of metals of into the inner matrix. Both mechanisms can also occur. In small concentrations, the traces of heavy metals in plants or animals are not toxic. Lead, Cadmium and Mercury are exceptions; they are toxic even in low concentrations. Monitoring of the contamination of soil with heavy metals is of interest due to their influence on ground water and also on plants, animals and humans (Fagbote and Olanipekun, 2010).

Accumulation of metals in plants is highly dependent on their availability in soil. Availability is defined as a dynamic three-step process involving a physio-chemically driven desorption process, a physiologically driven uptake process and a toxico-dynamic redistribution process within the body. Partitioning of metals over the solid phases and soil solution is affected by soil characteristics of which the pH is the most important. Environmental pollution and exposure to toxic material is an increasingly serious problem all over the world. The non-scientific use of hazardous materials in agriculture and industries and its dumping has created a great risk to human life, plants and animals. Similarly the heavy metals are assimilated in the environment from vehicle exhaust, from the smoke of industries or the spreading of industrial effluents through water in soil (Khan et al., 2007).

Heavy metal pollution can be defined as an undesirable change in the physical, chemical or biological characteristics of land, water and air that may or will harmfully affect animals and plants. Heavy metals have received the attention of researchers all over the world, mainly due to their harmful effects on plants (especially those on vegetative and generative parts of the plants). The presence of heavy metals in different foods constitutes serious health hazards, depending on their relative levels. For example, cadmium and mercury injure the kidney and cause symptoms of chronic toxicity, including impaired kidney function, poor reproductive capacity, hypertension, tumors and hepatic dysfunction. Lead causes renal failure and liver damage. Some other metals (e.g. chromium, zinc and copper) can cause nephritis, anuria and extensive kidney lesions. Therefore, the problem of food contamination (including fish) by toxic metals is receiving global attention (Tahan and Keltoum, 2011).

Heavy metals such as lead, cadmium, zinc, copper or arsenic are emitted from the earth's crust into the soil, air and water environmental media by anthropogenic sources such as non-ferrous metal industry or non-renewable energy consumption. The main problem with these substances is that, even at low soil concentrations, they can lead to major damage to human health or to ecosystem stability. To deal with this issue, the European Union has taken numerous initiatives. For example, the EU council signed the 1979 Convention on Long-range Transboundary Air Pollution on Heavy Metals in 2001. Several studies have investigated the impacts of heavy metals on trees and plants, but their impacts on ecosystems are still little understood. For the first time, an international team of researchers has investigated the effects of heavy metal soil pollution on young forest ecosystems. 32 replicates of a constructed model ecosystem (including 4 European forest trees species, and herbaceous and under storey plants from Europe) were installed in open-top chambers and kept under natural temperature and light conditions. The researchers used two types of soil: calcareous and acidic. To examine the potential effect of heavy metals and acid rain, they treated the ecosystems with acid (pH 3.5) or ambient (pH 5.5) rain and with or without heavy metal pollution (copper, zinc, cadmium and lead). After three years of processing and analyses, they evaluated the effects of these treatments. The results are as follows:

- Except for one of the four tree species investigated, fine root biomass decreased under the metal treatment.
- Total leaf area per tree was slightly reduced by heavy metal pollution.
- Heavy metal pollution also reduced water use efficiency of each species.
- Acidic soil inhibited above- and below-ground growth for two of the four tree species.

Overall, the researchers observed that the potential impacts of acid rain and HM pollution in soil on forests depend upon the type of plant species and type of soil. They also observed that climate conditions such as drought could enhance the impacts of pollutions. Acid rain was not found to have any substantial effect. These results can help us to understand the impacts of acid rain and heavy metal pollution on forests and might be helpful when making decisions for forest and ecosystem protection. Furthermore, the results may contribute to the development of new rehabilitation technologies. Indeed, this study provides crucial information on the most resistant species to heavy metal pollution depending on the soil and climatic conditions, information that can be used to better design rehabilitation of polluted soils (Anonymous, 2007).

Heavy metal pollutions have increased because of development of industries and air pollutions in Turkey in the last years. However the heavy metals are serious problems according to the last data obtained from forest, agriculture and urban areas in Turkey. High amount of heavy metals (Cd, Co, Pb, Ni etc.) were found in the natural forest resources and agriculture areas. The drying occurred because of heavy metal pollutions in the spruce and beech forests in the north-west of Turkey (Bağdat and Eid, 2007).

The ecological balance was affected because of industrial developments and intensively public demands for products and services from natural resources. In this context, the forests have very positive impacts owing to their products and services and fight against the deterioration of ecological balance. In this respect the continuity of forests is the common duty of the entire world's humanity. However, the presence of forest resources is under threat because of negative impact of biotic and abiotic factors such as forest fires, illegal cuttings, acid rains, insects, storms and snow. Turkey is a rich country in relation to forest resources. There is a large number of broadleaved and coniferous forest tree species in our natural resources. Uludag fir is one of these species with a wide natural distribution range. There is a wide use of Uludag fir because its wood is valuable, can be used as Christmas tree and the species has high landscape value.

The aim of this paper is to determine the changes of heavy metal pollutions in both needles and soil in pure Uludag fir forest resources in Bartın-Ardıç district according to the 3 altitude levels.

Material and Method

Material

Forests of the Ardıç district are situated in the *Northwest Euxinic* forest subzone of the *Euxinic* forest zone (Mayer and Aksoy, 1998). According to the inventory data of 2011, the otal forest area in the region is 12,456 ha, of which 28.6% is degraded forest. General soil type is stony, alkaline, sandy clay and sandy clayish mud of mediocre depth. Ardıç district is under the effect of Western Black Sea sub-climate (IIc). All seasons are rainy, the month with the highest mean rainfall is December (198.4 mm), the one with the lowest is June (53.0 mm). The mean annual temperature is 8.3 °C, the coldest month is January and the hottest month is July. The vegetation period is 6 months in the research area (May–October) (OGM, 2011).

Method

In this study carried out in pure Uludağ fir forests in Bartın-Ardıç district the change of amount of heavy metal in both Uludag fir needles and soil depending on altitude level was investigated. For this reason, sample plots and sample trees were established in three different altitude levels (1,000 m, 1,100 m and 1,200 m). Sample plots and sample trees were established according to the random blocks method. Furthermore control trees and control soil sample points were established in each altitude level in similar ecological and stand conditions with sample plots in which needle and soil samples were collected. On the other hand, 3 control sample points and 3 sample trees were established depending on altitude levels. Information about sample plots is shown in Table 1.

Table 1. General information about sample plots

Number of Altitude Levels	Altitude (m)	Amount of Soil Sample Plots	Amount of Collected Needle Sample Trees
1	1,000	10	5
2	1,100	10	5
3	1,200	10	5

Samples were collected between June 2009 and July 2010. Shoots of several plant species as well as representative soil samples from the soil directly adjacent to the sampled plants (0-30 cm, topsoil layer) were collected, obtaining a total of 3 soil samples and 3 plants samples.

For a better preparation against contamination during sampling, soils were collected with plastic spatulas and stored in polypropylene boxes. After collection, pebbles and twigs were removed. All soil samples were taken by mixing six sub-samples from three sites of each plot at 0-30 cm depth. Each soil sample was air-dried and sieved to <2 mm for physico-chemical properties including pH, potassium (K), calcium (Ca), magnesium (Mg), sodium

(Na), $CaCO_3$, organic matter, total organic, heavy metals. Total K, Ca, Na and Mg concentrations were determined using flame emission after digestion of the composite samples with boiling 2 M HNO_3 for 2 hours.

The plant and soil samples were taken randomly across the field during summer June 2009, near the potential contamination sources (industrial plants, busy roads, residential areas, etc.). Plant samples collected from the field were washed under running tap water to remove adhered soils.

The metal analyses of samples (Cu, Fe, Zn, Mn, Cr, Pb, Cd, and Ni) were carried out by using an Inductively Coupled Plasma-Atomic Emission Spectrometry Standard reference (ICP-AES) (Tahar and Keltoum, 2011). The concentrations of heavy metals are expressed as mg/kg dry weight. The absorption wavelengths were 205.560 nm for Cr, 324.754 nm for Cu, 259.940 nm for Fe, 257.610 nm for Mn, 216.555 nm for Ni, 220.353 nm for Pb, 213,857 nm for Zn and 214.439 nm for Cd, respectively. Heavy metals threshold values, calculated by Eduardo et al. (2010) (Table 2) for natural forest soil and forest tree species (sprout, fir, beech, ash, etc.), were used for comparisons with heavy metal values obtained from soil and plant samples in Uludag fir forests in the Bartın-Ardıç district.

Table 2. Threshold values of heavy metals in soil and trees (Eduardo et al., 2010)

Heavy Metals	Threshold Values (mg/kg)	
	In Soil	In Trees
Pb	100-400	1-50
Zn	20-300	100-400
Ni	1-100	1-10
Cu	50-100	1-20
Cd	1-3	0.01-1
Mn	1-60	1-60
Cr	1-150	0.5-2
Fe	1-1,000	500-1,500

SPSS (Statistical Package for Social Science) 9.0 pack program was used for the statistical analysis of all data obtained from the needle and soil samples. Kolmogorov-Smirnov test has been applied to determine whether the data had displayed normal distribution. Furthermore, the changes of heavy metals in Uludag fir forests depending on altitude levels were investigated using ANOVA and Duncan tests at $p<0.01$ at significance level.

Results and Discussion

Heavy metals are chemical elements common to all types of soils, and their abundance ranks between percentage (iron only) and parts per million. The very low general level of their content in soil and plants, as well as the biological role of most of these chemical elements, has led them being grouped under the generic name of 'micro elements'. When the soil has a very high content of such chemical elements, the term 'heavy metal pollution' is used. Hence heavy metals are synonymous to pollution and toxicity. The determination of heavy metals in soils was carried out for the measurement of total element content and to assess the base line knowledge of soil components with respect to which changes in soil composition are produced by vehicle pollution and agricultural inputs in the surrounding fields (Kiikkila, 2003; Oancea et al., 2005; Tahar and Keltoum, 2011). Soil and plant contamination by heavy metals is increasing nowadays. In the present study, the heavy metals (Pb, Zn, Ni, Cu, Cd, Mn, Cr, and Fe) concentration had decreased with the increase in altitude (Table 3 and Table 4).

The highest levels of Cd, Cr and Fe were found in the composite soil adjacent to the 1,000 m and other altitude levels. On the other hand these elements were found in the soil samples within the normal range in the 1,100 m and 1,200 m altitude levels. But there are significant differences at the $P<0.01$ level according to the results of ANOVA in respect to the amount of heavy metals depending on altitude levels. According to the results of Duncan test, three different groups were found (with the exception of Cd) when considering the changes of the amount of heavy metals in soil depending on the altitude levels at the $P<0.01$ significance level (Table 3). In a research carried out by Yang et al. (2003) in China, it was confirmed that the heavy metals (Pb, Ni, Cd, Cr, and Mn) concentration had decreased with the increase of altitude. The state of the research area is due to the pollution occurring from the Çatalağzı Power Plant in Zonguldak region and Iron-Steel Factory in Karabük region.

Table 3. The results of ANOVA and Duncan test on the amount of heavy metals in soil depending on altitude levels

Heavy Metals	Altitude Levels (m)	Amount of Heavy Metals (mg/kg)	F Values
Pb	1,000	34.21a	33.87***
	1,100	22.65b	
	1,200	17.53c	
Zn	1,000	22.34a	20.88***
	1,100	18.92b	
	1,200	13.75c	
Ni	1,000	11.05a	10.96***
	1,100	8.62b	
	1,200	5.48c	
Cu	1,000	18.76a	16.91***
	1,100	13.42b	
	1,200	10.84c	
Cd	1,000	2.41a	2.35***
	1,100	2.18a	
	1,200	1.13b	
Mn	1,000	21.56a	19.79***
	1,100	18.48b	
	1,200	13.27c	
Cr	1,000	71.56a	69.95***
	1,100	53.48b	
	1,200	37.13c	
Fe	1,000	1316a	1018.2***
	1,100	894b	
	1,200	678c	

******:*** *P<0.01 significance level*
a, b, c: *Same letters indicate similar groups*

The highest levels of Cd, Cr and Fe were found in the composite needle of Uludag fir adjacent to the 1,000 m and other altitude levels. On the other hand these elements were found in the needle samples within the normal range in the 1,100 m and 1,200 m altitude levels. But there are significant differences at the $P<0.01$ level according to the results of ANOVA in respect to the amount of heavy metals depending on altitude levels. According to the results of Duncan test, three different groups were found (with the exception of Cd) when taking into account the changes of the amount of heavy metals in needle of Uludag fir depending on the altitude levels at the $P<0.01$ significance level (Table 4).

Similarly, according to the results obtained from a research work on the effects of heavy metals on plant growth and photosynthetic activity, the amounts of Cr, Fe, Cd, Ni and Cu were found at high levels. In this respect, heavy metals are deposed in the top soil (0-30 cm depth) and can be absorbed by tree roots easily in the affected air pollution areas (Oancea et al., 2005; Behbahaninia et al., 2009). One can be said that the high amounts of heavy metals occurred at lower altitude (1,000 m in the research area) because of the effects of strongly precipitation and wind in the higher altitude ranges (1,100 m and 1,200 m in the research area). Furthermore, higher amounts of heavy metals are deposited in Uludag fir at 1,000 m altitude because of the proximity of Çatalağzı Power Plant in Zonguldak region and Iron-Steel Factory in Karabük region at 1,000 m altitude. However, toxic gases, as an output from the industrial companies, are more present at 1,000 m altitude in the Ardıç vicinity.

Table 4. The results of ANOVA and Duncan test on the amount of heavy metals in needles of Uludag fir depending on altitude levels

Heavy Metals	Altitude Range (m)	Amount of Heavy Metals (mg/kg)	F Values
Pb	1,000	13.32a	11.93***
	1,100	9.98b	
	1,200	4.71c	
Zn	1,000	115.43a	98.71***
	1,100	71.56b	
	1,200	54.48c	
Ni	1,000	6.53a	5.86***
	1,100	4.95b	
	1,200	2.34c	
Cu	1,000	16.45a	14.71***
	1,100	11.37b	
	1,200	6.58c	
Cd	1,000	0.87a	0.82***
	1,100	0.76a	
	1,200	0.15b	
Mn	1,000	15.43a	13.57***
	1,100	10.78b	
	1,200	7.66c	
Cr	1,000	1.86a	1.73***
	1,100	1.34b	
	1,200	0.52c	
Fe	1,000	1342a	1208.4***
	1,100	713b	
	1,200	348c	

******:*** *P<0.01 significance level*
a, b, c: *Same letters indicate similar groups*

Conclusion

The determined contents of heavy metals in the layer of soil down to 30 cm depth do not originate from ore mineralization in this region because the heavy metals exist at much deeper levels. On the contrary they are the consequence of precipitation of airborne particles and aero-sediments from the air over many years, which originated from the oxidation roasting and smelting of the copper concentrate containing heavy metals. This was proved after analyzing the soil samples obtained at greater distances from the smelting plant.

The determined heavy metal contents (Cd, Cr and Fe) in the soil and needles of Uludag fir in the studied area of the Ardıç region indicate a small degree of soil degradation.

In this context, the area should be carefully monitored in order to detect changes in the long-term risk due to the presence of elevated concentrations of trace elements in soils. Toxicological tests and risk assessment will also be carried out with newly polluted soils and trees (Uludag fir) from this site to evaluate the present environmental risk of trace elements and their transfer to the food chain. The grape plant alimentary behaved as a metal indicator for Pb, Mn, Zn, Fe, Cu, Cr, and Cd, indicating that it can be used for testing changes in metal availability in soils. The concentrations of metals in both plant species exceeded the limits established for humans and grazing animals which imply a health risk linked with the spread of pollution from mining sites to Uludag fir forests in the Ardıç district.

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