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Heavy Metal Contents of *Pinus Radiata* Trees of İzmit (Turkey)

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A comparative investigation of the heavy metal contents, Pb, Cd, Ni, Zn, Cu, Fe and Mn of the leaves of the samples collected from *Pinus radiata* and forest soils of İzmit (Turkey) has been carried out by atomic absorption spectrophotometry.

Key Words: Atomic absorption spectrophotometry, Environmental pollution, *Pinus radiata*, Fast-growing species.

INTRODUCTION

One of the most important factors influencing the growth of plants is the elements. The decrease in amount of some particular elements causes malnutrition in plants. On the other hand, increase in the amount of some elements, especially heavy metals, has hazardous effects. In addition, heavy metals give rise to deposit by industrial and transportation pollutants in the environment. Among the toxic elements, lead is naturally present in soils in the range of 15 to 40 ppm. At these levels it presents no danger to humans or plants. Soil pollution with lead based paints and the tetrahedral lead of past automotive fuels have increased soil lead levels to several thousand ppm in some places.

Unless the total lead level in the soil exceeds 150 ppm, it is simply reported as low and can be considered safe. Values above 300 ppm are potentially dangerous to people. Cadmium is extremely toxic to both plants and animals. It is naturally present in soils at safely low levels (less than 1 ppm). Industrial discharges of cadmium, however, often cause municipal sewage sludge to contain elevated levels of cadmium. Composted sludges are often used as soil amendments. Although safe upper limits of cadmium for both plants and animals have not been established, monitoring soil cadmium levels helps to avoid excesses when such materials are used. Unless the cadmium in soil exceeds 1 ppm it is not considered harmful[1].

A number of studies of the trace metal concentrations in pinus species, especially in Finland and Japan, have been carried out in recent years. Arduini *et*

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al.[2] reported to have found that cadmium and copper affected the growth of *Pinus pinea* by decreasing its biomass to a remarkable extent.

Takeda *et al.*[3] investigated the metal concentrations of red pines (Japan, Honshu island) and found these higher in and near industrial regions than in non-industrial zones. Kurczynska *et al.*[4] reported the higher values of metal concentrations in Scots Pinus near the polluted area of Warsaw. Rantio *et al.*[5] reported the effect of sulfur, copper, and nickel on the chemical composition of Scots Pinus and found the levels of these metals higher near the metal moulding plants in Monchegorsk.

In another work, Larsson *et al.*[6] found Cu, Ni and Zn levels higher in Scots Pine trees around metal moulding plants in South-West Finland. The element contents of some pine species were reported[7–9]. More recent works on the elemental compositions of the various parts of the pinus and lichen species were reported[10–14].

There is a remarkable enviromental pollution in the area under discussion in this work since various and a great amount of pollutants are present contributing to the atmospheric, soil and water pollution in the Gulf of İzmit (Turkey) region. The pollution originating from both the industrial and concentrated anthropogenic activities threatens the forest and water resources of the region.

The objectives of this work were basically: (a) to determine the heavy metal contents of the leaves of *Pinus radiata* grown in the area under discussion; (b) to determine the heavy metal contents of the soils where the *Pinus radiata* species grow; and (c) to compare the values obtained from different crop areas.

EXPERIMENTAL

All chemicals were purchased from Merck (Darmstadt, Germany). A Shimadzu 6601 F model atomic absorption spectrophotometer was used to measure the element contents of the soil and leaf samples.

Pinus radiata, because it can grow even in poorer soils, is an important species for its fast-growing properties and usage in cellulose and paper industry. Its natural distribution zone is southern California. In Europe it is widely grown in Spain and Turkey. Leaf samplings were performed during 1998–99. From the four different regions of forest, samples were collected from three different trees of each region. The sample solutions were prepared at least three times for each tree for a specified period of time.

Analytical Procedures

Sampling of Soil Samples and Preparation for Analysis

The soil samples were collected twice from the soils of four different kinds in January and October 1998. From each soil three different tree species at 100 m distance apart were selected. In order for the soil to be represented well, the soil samples were taken from three diffrent depths *ca.* 0–5, 5–20 and 20–40 cm. The samples were put into plastic bags and air-dried on paper for 1 week. Then they were ground thoroughly in a mortar and sieved through a 0.5 mm net.

Solutions: Ammonium acetate (pH = 7.0) was prepared by mixing glacial acetic acid (57.5 mL) and ammonium hydroxide (60 mL) and diluting to 1000 mL. Extracting solution was prepared by mixing ammonium acetate solution, acetic acid 2.5% and 0.1 M HNO_3 (20 : 20 : 20; v/v/v).

Preparation of the soil solutions[16]: 5 g portion of the air-dried and ground soil sample was shaken with extracting solution (60 mL) for 2 h. The resulting solution was evaporated again to dryness. To the residue was added concentrated HNO_3 (5 mL) and evaporated to dryness. The residue was dissolved in 2 M HNO_3 (50 mL), filtered and diluted to 100 mL. Then, the element concentrations were de The working conditions for AAS are given in Table-1.

TABLE-1
WORKING CONDITIONS FOR AAS

Element	Wavelength (nm)	Slit width	Flow rate (L/min)
Pb	283.3	0.5	2.0
Cd	228.8	0.5	1.8
Cu	324.8	0.5	1.8
Zn	213.9	0.5	2.0
Ni	232.0	0.2	2.2
Mn	79.52	0.2	2.0
Fe	248.3	0.2	2.2

Preparation of leaf samples by wet digestion:

Solutions: Acid mixture were prepared by mixing concentrated nitric acid (1000 mL), concentrated suphuric acid (100 mL) and 60% perchloric acid (40 mL).

Procedure: To a 5 g portion of finely grounded and dried leaves was added concentrated nitric acid (5 mL) and the mixture was heated on a water-bath for 1 h. Then it was evaporated on a hot plate. Acid mixture (25 mL) was added to this residue and continued to evaporate until all the acid smokes ceased. The residual mixture was dissolved in distilled water (20 mL), filtered and made up to 100 mL. After 6 h, it was filtered again to remove the silisium. The resulting solution was injected into the flame to measure the metal concentrations[15]. Table-1 shows the results obtained. The values are average S.D. for n = 10 measurements.

RESULTS AND DISCUSSION

İzmit is one of the major industrial zones of Turkey where an approximate 15% of the total industrial production including automotives, dye, oil refinery, textile, polymeric materials, pharmaceuticals is being done. In addition, marine traffic in the Gulf of İzmit which takes second place among the harbours of Turkey is very crowded due to this industrial activity. Moreover, since it is a cross point of the Turkish and international highway transportation, İzmit has been facing the environmental pollution problems most effectively since the early 1960s. Accordingly, this pollution affects the forests around. We, therefore, are focused on investigating if the *Pinus radiata* species planted in Kerpe, İzmit would be affected by the heavy metal pollution.

In this work, the elements Pb, Cd, Ni, Zn, Cu, Fe and Mn were determined both in needles of the trees (Table-2) and in the soils (Table-3) where they were planted. Of the elements analyzed, Pb, Cd, Ni, Zn, Cu are anthropogenic originated and Mn, Fe are anthropogenic and soil originated.

The normal element levels of *Pinus radiata* grown in Northern America were reported[17, 18] as 50–267 ppm (Fe), 3–46 ppm (Cu), 36–1500 ppm (Mn), 19–250 ppm (Zn), 7–40 ppm (Ni).

In a comparison of our values with the literature values above, it can be seen that Cu, Fe, Mn levels are within the above literature values and Zn is lower, while Ni is higher than these values. Since lead and cadmium are highly toxic elements, we may consider that these elements have accumulated even though in small amounts.

With respect to the values obtained by following up the metal contents of the needles in the four different seasons, all the metal contents were found higher in winter. This result may be attributed to higher chimney emissions in winter season in comparison with summer season.

When the values obtained by analyzing the metal contents of the soils where the *Pinus radiata* species grown up are evaluated, in general, element levels are found to be closely same for both November and January. This may be attributed to the fact that there is no remarkable difference of rainfall in these months to contribute to the metal deposition.

TABLE-2
ELEMENT CONTENTS OF *PINUS RADIATA* LEAVES (ppm)[a]

Element	March	June	September	December
Pb	2.4 ± 0.17	2.1 ± 0.18	2.3 ± 0.22	2.7 ± 0.60
Cd	0.2 ± 0.08	0.4 ± 0.06	0.7 ± 0.12	0.8 ± 0.11
Ni	34.0 ± 6.0	54.0 ± 7.10	80.5 ± 7.40	84.2 ± 9.1
Zn	6.6 ± 0.35	4.3 ± 0.40	6.7 ± 0.54	8.0 ± 0.88
Cu	3.4 ± 0.25	4.2 ± 0.35	4.9 ± 0.32	6.5 ± 0.69
Fe	41.0 ± 5.30	33.4 ± 4.90	54.5 ± 6.60	56.5 ± 7.2
Mn	155.7 ± 12.10	113.0 ± 10.50	156.8 ± 15.4	169.6 ± 14.7

[a] Average value standard deviation of ten measurements.

As for the values obtained from the deeper soils, some element levels of the soils taken from a 20–40 cm depth were found lower than those of surface soil values. The acceptable heavy metal levels in soil are given as for Cu, 50 ppm; Zn, 30 ppm; Cd, 3 ppm; Pb, 100 ppm; Ni, 50 ppm19. Of the values given in this work, lead, nickel, zinc and copper levels are seen to be within the range in literature. Manganese and iron levels in soil were reported1, 19 as 20–800 ppm for Mn and 118–672 ppm for Fe. Cadmium level is found generally higher.

TABLE- 3
ELEMENT CONTENTS OF THE SOIL WHERE *PINUS RADIATA* GROWS (ppm)

Sample collection part	Pb	Cd	Ni	Zn	Cu	Fe	Mn
	January						
0–5 cm depth	2.1* 18.0† 9.9‡	1.3 10.6 3.6	5.5 108.0 25.9	3.8 30.8 13.0	1.3 7.1 3.6	58 1500 584	93 119 112
5–20 cm depth	2.2 18.1 10.3	1.2 7.7 3.3	1.4 162.0 30.9	6.1 31.4 11.7	1.5 5.8 3.1	76 664 400	84 119 110
20–40 cm depth	3.0 14.3 7.8	0.8 9.2 3.5	6.0 84.0 24.2	2.2 24.4 11.3	1.6 7.4 3.9	68 808 395	11 117 60
	November						
0–5 cm depth	9.5 15.7 12.9	0.5 5.7 2.1	7.7 64.0 23.8	0.5 32.6 10.0	1.2 5.5 2.4	324 768 548	33 93 76
5–20 cm depth	9.6 14.6 12.4	0.5 3.8 1.6	8.0 80.0 22.6	2.8 32.0 14.2	1.1 5.8 2.9	80 676 386	18 72 52
20–40 cm depth	7.0 15.0 11.4	0.6 3.5 1.6	9.2 96.0 28.6	2.4 24.0 11.1	0.5 5.8 2.9	44 724 375	20 80 50

*minimal , †maxima, ‡average.

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