The Determination of Metal Accumulation in Firethorn (*Pyracantha Coccinea* M. Roemer) Leaves in Eskisehir (Turkey)

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Summary: In this study, firethorn plant (*Pyracantha coccinea* M. Roemer), a prevalent shrub in Eskişehir (Turkey) city, was used to monitor the influence of metal pollution caused by traffic. Samples were collected in the fall and winter seasons from ten locations. The concentration of heavy metals (Cu, Cd, Cr, Fe, Ni, Pb and Zn) was determined from plant leaves. Besides, metal contents were examined in the surface soil (0–30 cm) samples collected from each location. The heavy metals determined from leaves and soil was evaluated statistically against motorized vehicles number. A meaningful correlation between heavy metal concentrations in plant and soil samples and vehicles number was determined. In addition, the metal concentrations in firethorn leaves have been compared with the critical heavy metal values in the literature. The mean metal (Cd, Cr, Fe, Ni and Pb) concentrations were found higher than the limit values. According to the metal studied the highest Cu, Fe, Zn, Cd and Pb concentrations for firethorn leaves are found in the Ankara-Istanbul intercity highway (location 2) and the highest Cr and Ni levels are found in the main gate of Anadolu University, intercity highway (location 9). It was clearly found that human and other living organisms are under the risk of heavy metal pollution.

Introduction

Urban areas are exposed to numerous airborne contaminants emitted from anthropogenic sources in the form of solid particles or gases. The main sources of these pollutants are industrial plants, power stations, domestic heating systems and motor vehicles, the last two usually being prominent in urban areas [1]. Traffic pollution, contamination due to high levels of traffic, caused mainly by the burning of fossil fuels, primarily oil in the form of petrol and diesel. The most prevalent pollutants from traffic are carbon monoxide, nitrogenous oxides, heavy metals, volatile organic compounds, and particulates.

Several studies on plants in relation to air pollution and metal deposition in different regions of the world have been carried out [2-5]. Biomonitoring, based on the analysis of trace elements in plants like lichens, mosses, deciduous tree leaves and conifer needles has been proposed as a solution to the air pollution monitoring problem. Leaves with large surface areas per unit of weight and/or a long lifespan, like conifer needles or evergreen tree leaves, are considered to be good accumulators. Representative results may be obtained using standardized biomonitors which in general reflect both air and soil pollution [1, 2]. Chiefly, biomonitoring studies are based on the estimation of trace elements concentration originated from industry, settlement or traffic emissions [3-6]. Vegetation is an effective indicator of the impact of a pollution source in its vicinity because most plants have the ability to accumulate heavy metals. Furthermore, may be more reliable than that obtained from direct determination of the pollutant concentrations in air over a short period. Hence analysing plant tissues can give better results in terms of sensitivity and reproducibility [7].

The city of Eskisehir is located in the northwest Turkey, 29° 58' and 32° 04' E and 39° 06' and 40° 09' N. The topographic structure of Eskişehir consists of plain areas and surrounding mountains in Sakarya and Porsuk river basin. Bozdag and Sündiken mountains encircle the river basin plain areas at north, Turkmen mountains, Yazılıkaya plateau and Emirdag at west and south. The surface area includes 21.8 % of mountain, 25.8 % of plain and 52.4 % of plateau. Although regional climate is close to the transition climate between west Anatolian climates, it is generally severe, cold and snowy in the winter, hot and dry in the summer. The duration of rainy season in this region is approximately 100 days in a year and it is for short time. The average rainfall is 373.6-450 mm/m^2. Annual average temperature is 10°C. Although the winds generally blow in from no direction, they are prevailing in east direction in winter, in west in other seasons, and at spring times cause rainfall [8]. The province covers an area of 2.678 km^2, as of 2007 the city had a population of 600.000. Eskişehir is one of the largest industrial centers of Turkey, with several modern industries, producing trucks, home appliances, railway locomotives, fighter aircraft engine, agricultural equipment, textiles, brick, cement, chemicals, processed meerschaum and refined sugar.

During this study metal pollution in the province of Eskişehir (Turkey) has been analyzed using firethorn (*Pyracantha coccinea* M.Roemer) leaves exposed in urban sites subjected to vehicular traffic. In this study period, 163.723 (October 2007) and 165.760 (February 2008) automobiles were officially registered in Eskişehir province [9]. The data obtained may indicate potential risk areas for human and other organisms (plants, animals and microorganisms) living in the city and a for metal pollution risks in the future.

Results and Discussion

This study was conducted at 10 locations, and Tables 1-2 show average concentrations of metal in firethorn leaves and soils. Cu, Ni and Pb concentrations in the Odunpazarı, Bademlik Road (location 1) are lower than in other locations. This locality has the lowest traffic density in the study area. The highest Cu, Fe, Zn, Cd, and Pb concentrations for leaves are found in the Ankara-Istanbul intercity highway (location 2) and the highest Cr and Ni levels are found in the main gate of Anadolu University, intercity highway (location 9). Therefore, the highway with the high traffic density represents a risk for the living organisms.

The lowest copper concentrations in leaves and soils were measured at the 1st location. It is known that the source of copper on plants from roadside is street dust and abrasion of metal part [10]. The lowest iron leaves quantities were measured at the 1st and 6th locations. Zinc lower quantities were measured in the 7th and 8th locations. The automobiles cause about half of zinc and iron contribution to the environment from urbanization. Brakes are releasing copper; auto body rust and engine parts are releasing iron. Motor oil is tending also to accumulate metals as it comes in contact with surrounding parts as the engine runs, so oil leaks becomes another pathway by which metal is entering the environment. Since the heavy metal does not degrade naturally, accumulation of high concentration in soils can be toxic to organisms living in surrounding environments [11].

The heavy metals concentrations of cadmium, chromium, nickel and lead increase according to the traffic density increasing. It is

Table-1: The heavy metal concentrations in firethorn leaf samples (mean values ± standard deviation).

Location Number	Parameters (mg kg^{-1} dry weight)						
	Cu	Fe	Zn	Cd	Cr	Ni	Pb
1	3.88 ± 2.080	139 ± 74.531	57 ± 25.922	2.46± 1.458	2.18± 2.200	17.42± 6.068	66.6± 14.380
2	31.92± 43.78	509.4± 157.787	69.4 ± 22.645	5.42± 3.142	10.04± 10.568	35± 35.362	94± 7.615
3	10.32 ± 3.068	324± 126.757	56.8 ± 18.033	2.33± 0.992	4.53± 7.554	43.4± 35.267	83.4± 14.570
4	5.40 ± 1.842	248± 92.032	55.4 ± 23.136	2.06± 0.614	1.54± 1.545	25.36± 14.551	81.2± 6.906
5	21.82 ± 28.557	236.8± 85.578	56.2 ± 12.111	2.40± 1.081	2.73± 3.064	27± 15.811	67.6± 19.514
6	7.80 ± 5.283	114± 46.824	62.8 ± 20.789	2.44± 0.928	1.22± 0.614	18.6± 2.607	63.6± 16.009
7	9.48 ± 5.142	241.4± 96.552	43.8 ± 6.418	2.04± 0.391	2.44± 2.469	32.2± 8.105	78.6± 14.774
8	6.12 ± 2.943	181± 78.294	38.7 ± 24.299	2.04± 0.978	0.64± 0.194	25.3± 30.584	74.8± 9.731
9	10.68 ± 7.452	202± 122.963	65 ± 21.494	5.20± 0.626	12.52± 6.414	52.4± 31.643	83.8± 21.405
10	9.87 ± 2.984	420.6± 218.138	65 ± 19.761	3.42± 2.903	6.116± 6.432	47.2± 36.519	70.2± 10.353

Table-2: The average heavy metal concentrations in soil samples (mean values ± standard deviation).

Location Number	Parameters (mg kg^{-1} dry weight)						
	Cu	Fe	Zn	Cd	Cr	Ni	Pb
1	67.40 ± 7.873	2955.14± 525.084	64.55± 17.674	4.34±1.548	32.57±6.143	86.76±19.670	135±53.225
2	160.13± 43.984	4143.25± 1096.208	150.25± 42.758	7.03±2.444	65.83±8.792	196.68±8.019	421.88±65.375
3	176.99± 22.390	5333.1± 403.714	122.96± 15.506	3.68±1.140	48.87±3.058	266.1±40.672	241.45±11.608
4	92.7± 6.516	2961.227± 289.095	80.89± 13.064	4.34±0.670	32.57±2.970	202.46±16.598	161.8±45.222
5	117.98± 15.428	6472.75± 881.246	88.87± 38.966	5.93±1.300	163.7±47.401	381.82±32.110	181.18±18.389
6	75.233± 21.202	3560± 624.261	76± 25.005	5.78±1.353	65.17±20.610	121.47±18.483	120±21.558
7	236± 54.147	4654.9± 897.139	63± 10.133	5.78±0.460	65.17±3.546	214.03±3.568	341.76±51.238
8	84.27± 22.067	2415.2± 778.362	58.62± 16.153	3.61±1.351	32.57±11.423	167.75±18.437	100.65±33.444
9	168.533± 7.018	5940.15± 1786.454	145± 19.672	10.74±3.428	97.78±9.480	352.89±49.932	341.76±38.738
10	84.27± 28.919	3862.5± 1586.659	112± 18.553	5.78±1.760	48.87±8.896	306.6±25.637	181.18±27.473

known that cadmium comes from the tires, oils and other equipments of the vehicles [12]. Nickel pollution on a local scale is caused by the emission from motorized vehicles, which are using nickel gasoline, and also by abrasíon and corrosion of nickel from vehicle parts. The chromium pollution is caused by the abrasion of chromium plated vehicle parts. Lead is released from the exhaust of the motorized vehicles to the atmosphere in a much higher quantity than other sources [13-14].

On comparison of critical heavy metal values and normal values given in the literature with our results of firethorn leaves, it become clear that Cd, Cr, Fe, Ni and Pb levels exceeded the limits (Table-3). The mean accumulation levels of heavy metal in soil were compared to critical heavy metal values. The critical heavy metal values (mg kg^{-1}) in soil [15-18] is as follows: Cu (50-125), Cd (3), Cr (50-200), Fe (50), Ni (50), Pb (100) and Zn (300). According to heavy metal analyses in soil, Fe, Cd, Ni and Pb levels exceeded the critical limits. Zn and Cr levels were above the limits and Cu levels exceeded the limits in 2^{nd}, 3^{rd} and 9^{th} localities.

Statistical Analyses and Data Treatment

Correlation Coefficient Analysis

The relationship between heavy metal levels of traffic density and firethorn leaves was supported by the Pearson correlation index (Table-4). There was a positive correlation between chromium concentration in leaves and vehicle numbers ($r = 0.584$; $P <= 0.01$; n = 50 for firethorn, excluding site 10); there was also a significant correlation between iron, nickel, lead and cadmium in leaves and vehicle numbers. This indicates that the origin of the metals in the investigated area is related to the traffic density. Also, it was found that the relation between; Cu, Fe, Ni, and Cd level in soil samples and vehicle number were directly proportional. There was a highly significant correlation Pb ($r = 0.801$; $P <= 0.01$, n = 30 for soil, excluding site 10) and Zn ($r = 0.976$; $P <= 0.01$) levels in soil and vehicle numbers. Besides, there was a positive correlation between Ni ($r = 0.319$; $P <= 0.05$), Pb ($r = 0.458$; $P <= 0.05$) and Zn ($r = 0.338$; $P <= 0.05$) concentration in leaves and soil samples.

Table-3: The metal concentrations in firethorn leaves and critical heavy metal values in plants.

	Parameters						
	Cu	Fe	Zn	Cd	Cr	Ni	Pb
[a]Critical heavy metal values for plant (mg kg^{-1})	100	50 - 200	80 - 200	5	5 - 10	25 - 40	30
[b]Normal content (ppm)	10	-	50	0.05	1.5	-	1
[c]Normal levels (mg kg^{-1})	3-20	30-300	15-150	0.1-1	-	0.1-5	2-5
[c]Phytotoxic levels (mg kg^{-1})	25-40	-	500-1500	5-700	-	50-100	-
Min.-Max. heavy metal concentration for plants in this study (mg kg^{-1})	3.88-31.92	114-509.4	38.7-69.4	2.04-5.42	0.64-12.52	17.42-52.4	63.6-94

According to [a] [15- 18], [b] [20], [c][21]

Table-4: Correlation of traffic density and metals contents in firethorn leaf (n: 50) and soil samples (n: 30).

	Metals														
	Vehicle number	Cu (S)	Cu (L)	Cr (S)	Cr (L)	Fe (S)	Fe (L)	Ni (S)	Ni (L)	Pb (S)	Pb (L)	Zn (S)	Zn (L)	Cd (S)	Cd (L)
Vehicle number	1.000														
Cu (S)	0.531**	1.000													
Cu (L)	0.297*	0.155	1.000												
Cr (S)	0.272	0.238	0.253	1.000											
Cr (L)	0.584**	0.253	0.556**	0.157	1.000										
Fe (S)	0.582**	0.581**	0.217	0.833**	0.307*	1.000									
Fe (L)	0.487**	0.223	0.450**	-0.015	0.362**	0.118	1.000								
Ni (S)	0.542**	0.352	0.168	0.711**	0.308*	0.819**	0.236	1.000							
Ni (L)	0.360*	0.224	-0.099	0.068	0.045	0.243	0.427**	0.319*	1.000						
Pb (S)	0.801**	0.819**	0.302*	0.229	0.479**	0.493**	0.434**	0.318*	0.256	1.000					
Pb (L)	0.433**	0.356*	0.090	-0.070	0.221	0.101	0.348*	0.104	0.240	0.458*	1.000				
Zn (S)	0.976**	0.347*	0.288*	0.239	0.578**	0.514**	0.498**	0.516**	0.245*	0.686**	0.384**	1.000			
Zn (L)	0.281*	-0.046	0.279*	0.092	0.155	0.128	0.140	0.098	-0.001	0.155	0.018	0.338*	1.000		
Cd (S)	0.656**	0.349*	0.167	0.499**	0.520**	0.549**	0.079	0.493**	0.251	0.615**	0.172	0.625**	0.242	1.000	
Cd (L)	0.399**	0.070	0.548**	0.040	0.557**	0.054	0.332*	0.050	-0.082	0.359*	0.205	0.423**	0.287*	0.250	1.000

* Significant at $P < 0.05$; **Significant at $P < 0.01$; S: Soil, L: Leaf

Experimental

Sampling and Chemical Analyses

Ten sampling sites were selected near the roadside having different traffic density (Table-5) and fairly far from industrial area and heavy metal sources in Eskişehir (Turkey). In each site, about 0.5 kg fresh leaves were detached from the shrub at 0.4-0.5 m above the ground. Heavy metal concentrations were also determined in soil samples (about 2 kg wet weight) collected from each location indicated in Fig. 1. Samples were taken from all sites at monthly basis (October 2007-February 2008). The number of motor vehicles within a locality was counted for 15 minutes in the morning, noon and evening and the average number of vehicles per day was worked out.

The leaf samples were dried at 105°C for 24h. Surface soil (0–30 cm depth) samples were dried at 105 °C for 3h. After grinding samples were passed through nylon sieves (0.5 mm), and 0.5 g of each sample was placed in pyrex reactors of a CEM Star 2 microwave digestion unit. Digestion was carried out using a mixture of concentrated HNO_3: $HClO_4$ in 3:1 proportion. Samples were mineralized at 140 °C for one hour. Afterwards, the samples were filtered in such a way as to make their volumes up to 100 mL with 0.1N HCl. Heavy metals concentrations were measured by Flame Atomic Absorption Spectrophotometer (FAAS, Varian Spectra A 250 Plus Model) [3,19]. In the FAAS analysis, the following wavelength lines were used; Ni 232.0 nm,

Table-5: Traffic density at different localities.

Locality number	Traffic density (vehicles/day)	Locality name
1	5800	Odunpazarı, Bademlik Road
2	57600	Ankara-Istanbul intercity highway
3	43000	Atatürk Street
4	15000	Centrum of Eskişehir
5	22300	Campus of Eskişehir Osmangazi University
6	11520	Road of Muttalıp Village
7	17500	Kütahya Road
8	7600	Seyitgazi Road
9	56500	Gate of Anadolu University, intercity highway
10	30250	Ankara Road

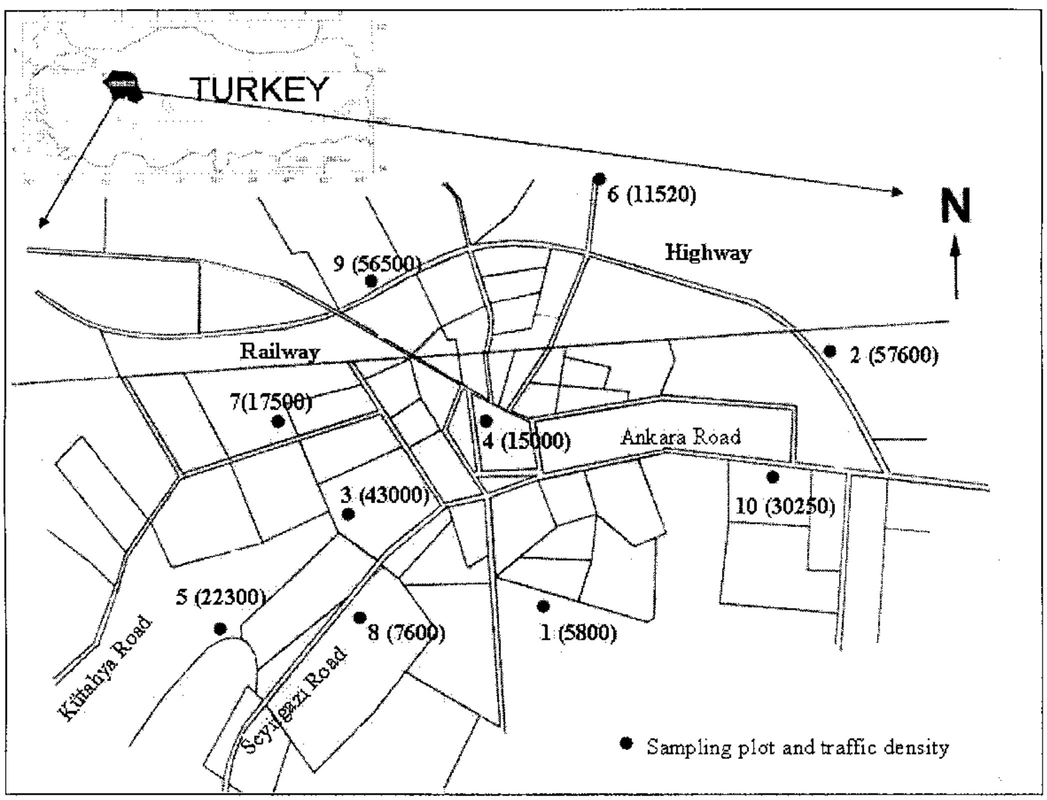

Fig. 1: Sampling plots and traffic density (vehicles / day in parenthesis).

Table-6: Analysis of the standard (NIST) and certified (NCS) reference materials (mg kg^{-1} dry matter).

Metal	NIST-SRM 1573a (leaves of tomato)		NCS DC73350 (leaves of poplar)	
	Certified	Analytical value	Certified	Analytical value
Cu	4.70 ± 0.14	4.85	9.3±1.0	10
Fe	368 ± 7	364	274±17	265
Ni	1.5 ± 0.07	1.51	1.9±0.3	1.85
Cr	1.99 ± 0.06	1.93	0.55±0.07	0.50
Pb	-	-	1.5±0.3	1.52
Zn	30.9 ± 0.7	31.8	37±3	33.5
Cd	1.52 ± 0.04	1.49	-	-

Fe 248.3 nm, Cu 324.8 nm, Cr 357.9 nm, Cd 228.8 nm, Pb 217.0/283.3 nm, and Zn 213.9 nm. The analytical process quality was also controlled by certified reference material of NCS DC73350 (leaves of poplar) and standard reference material NIST-SRM 1573a (leaves of tomato). The analysis of these standard reference materials showed good accuracy, with the recovery rates of the metals, between 90 % and 107 % (Table-6).

Statistical Analyses and Data Treatment

Pearson's correlation coefficient was used to measure the degree of correlation between logarithms of leaves, soils metal concentrations and vehicles number.

Conclusion

The result of this study indicated that the firethorn leaves growing in the city center of Eskişehir, have heavy metal in high concentrations. A meaningful correlation was found between the number of vehicles and heavy metals concentrations in leaves and soil samples. On the other hand, the heavy metals of Fe, Cd, Cr, Ni and Pb values obtained for firethorn leaves are higher than the critical heavy metal values for plants in literature. Also, Fe, Cd, Ni and Pb levels in soil are higher than the critical metal levels in literature. The location with high vehicle number affects negatively on living beings together with the plants. The disease risk, caused by the heavy metal pollution, increases especially for the people living or working in this area.

The main aim of the study to determine the usability of firethorns for detecting the heavy metal pollution caused by traffic. When the traffic density and the heavy metals amount in the leaves of firethorn were compared, it was revealed that this plant could be used for this purpose. Therefore, firethorn which can be obtained at any time of the year can be considered to be an indicator plant in terms of detecting the heavy metals pollution. In the mean time, a detection of the current situation was performed regarding the heavy metal pollution arising from the traffic in Eskişehir. Through the obtained data it was displayed that there was a relatively heavy metal pollution. This situation indicates that it is required to enhance the mass transportation by increasing the number of public transit vehicles (tramway, metro etc.) and that the authorities are required to immediately take measures. Additionally, it is required to enforce legal practices like controlling the entry of vehicles to the heavy traffic areas and imposing transit taxes. Together with these controls and practices it is suggested that further studies will/would be conducted that will demonstrate to what extent the currently detected pollution is assimilated by plants and natural cycles.

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