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Investigation of Spatial Variation of Air Pollution around an Industrial Region Using Trace Elements in Tree Components

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Abstract— As a consequence of atmospheric pollution, trace elements accumulate in forest ecosystems. Therefore, measurement of pollutants in tree barks and leaves/needles has been commonly used to determine the level and spatial distribution of air pollution in an area. The objective of this study was to determine the spatial distribution of various trace elements in Aliaga industrial region, Turkey. Leaf litter and tree component samples (bark, leaf/needle and branch) of two pine species (*Pinus brutia and Pinus pinea*) were collected at 27 different sampling sites. All collected samples were analyzed for several trace elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Tb, Th, Tl, U, V, Y, Yb, Zn) using ICP/MS techniques. Quality control and assurance procedures applied during the sampling, sample preparation and analysis. Highest concentrations of the anthropogenic trace elements were observed in leaf litter samples while the lowest ones were in branch samples. Concentrations of trace elements were substantially lower at background sites compared to those around industrial sources. The spatial distribution of anthropogenic trace element concentrations measured in tree components indicated that their major sources in the region were industrial activities (i.e., iron-steel production, petroleum refining, ship dismantling). Results of the present study also showed that tree components could be used as indicators of spatial variation of air pollution in a region.

Keywords— Air pollution, trace elements, tree components, Turkey.

I. INTRODUCTION

TRACE elements are natural components of the environment and they are emitted into the environment from transportation, industry, fossil fuels burning, agriculture, and other human activities [1]. They are persistent and widely dispersed in the environment and interacting with different natural components [2]. Most of the trace elements (P, K, Ca, Mg, Fe, Ma, Zn, Cu, Mo, Co, V) are essential elements to living organisms, but their excessive amounts are generally harmful to plants, animals and humans [3].

Plants have been used as biomonitors and bioindicators of atmospheric pollutants in urban, rural and industrial areas [4]. Plant biomonitoring is being increasingly used as an alternative to the traditional methods of studying regional deposition of natural and anthropogenic pollutants from the atmosphere to the terrestrial environments [5]. Plants provide information on the quantity of air pollutant concentrations and the effects of air pollution on living organisms [6].

Measurement of pollutants in tree barks and leaves/needles has been commonly used to determine the level of air pollution that the trees are exposed. By applying this approach it is possible to determine the spatial variation of air pollution in a region. There have been several studies that successfully monitored the trace elements in different tree components (bark, leaf/needle, and leaf litter) [2], [7], [8], [9].

A heavily industrialized region (Aliaga) located in the western part of Turkey was covered in this study. Aliaga region is one of the hot spots of the country because of the several major industries (petrochemical industry, petroleum refinery and steel plants with electric arc furnaces) and ship dismantling plants and ports that significantly contributes to the local air pollution [10], [11]. Therefore, the main objective of this study was to investigate the spatial variation of air pollution in Aliaga industrial region in Turkey by measuring trace elements deposited in tree components (i.e., bark,

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leaf/needle, branch) and leaf litter of two pine species (*Pinus brutia and Pinus pinea*)

II. EXPERIMENTAL

A. Sampling Program

The field studies were carried out in the forested areas of Aliaga industrial region. The sampling sites were selected based on the locations of industrial facilities, previous studies carried out in this region [10], [11], [12] and meteorological conditions. Red pine (*Pinus brutia*) and Stone pine (*Pinus pinea*) are the widespread species in the forested areas of Aliaga. Therefore, these species were sampled in the study. Pine needles (1 and 2 years of age), bark, branch, and leaf litter samples were collected from 27 sites during the period of September 26 – November 04, 2011.

B. Sampling Method and Analysis

Needle and branch samples were collected from the different directions and upper 1/3 part of each tree. Bark samples were collected from 1.5 meter in height and 3 different directions of selected trees. Leaf litter samples were collected at least at 4 different points in the each sampling site and they were integrated. Collected samples were brought to the laboratory and stored at 4°C until analysis.

Plant samples (0.5 g) were prepared for analysis using the acid digestion procedure. This was carried out in a closed vessel digestion system. A programmable 1600 W microwave (MARS 5, CEM Corp.) with a rotor for 40 Teflon (PFA) vessels rated 260 ºC and self regulating pressure control was used. The samples were placed in the vessels and then 7 ml of HNO_3 (65%, Merck), 3 ml of HCl (30%, Merck) and 2 ml of H_2O_2 (30%, Merck) were added. Capped Teflon vessels were placed in the microwave system and digested. The digestion program was applied in two steps; in the first step; the temperature was ramped to 150 ºC within 3 min followed by a hold time of 5 min, then the temperature was ramped to 180 ºC within 7 min followed by a hold time of 10 min. the vessels were then cooled to room temperature and the samples were diluted to 50 ml with Milli-Q deionized water (18.2 MΩ/cm) and then filtered through 0.45 µm PTFE Minisart SRP filters (Sartorius, Germany).

Samples were analyzed for 48 trace elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Tb, Th, Tl, U, V, Y, Yb, Zn) using an Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Agilent 7700x with ORS and HMI System) system.

III. RESULTS

The mean concentrations of several anthropogenic and crustal elements collected from industrial and background sites are given in Table I and Table II. All sample concentrations measured in this study were reported on dry weight (dw) basis.

Crustal element concentrations were comparable in industrial and background sites. However, anthropogenic element concentrations were substantially higher in industrial sites. Average concentrations (mg/kg, dry weight) of major anthropogenic elements (Pb, Fe, Zn and V) in different plant components in the industrial sites ranged between 7.5-159, 182-5663, 35.9-991, and 0.27-15.2 while in background sites they ranged between 0.73-2.4, 88.5-502, 8.5-33.3, 0.17-1.1, respectively. For crustal elements (Al, Ca, K, Mg, Sr), the concentration ranges (mg/kg, dry weight) in the industrial sites were 59.4-2002, 4907-19075, 632-11793, 691-3381, 12.5-44.2 (Table I) while in background sites ranges they were 97.3-531, 4311-11874, 460-9008, 453-2721, 11.6-36.1, respectively (Table II).

TABLE I

TRACE ELEMENT CONCENTRATIONS OF TREE COMPONENTS AND LEAF LITTER SAMPLES IN INDUSTRIAL SITES

Components	1-year needle	2-year needle	Branch	Bark	Leaf litter
INDUSTRIAL SITES					
Anthropogenic elements (mg/kg dw) (Mean± Std.dev.)					
Ag	0.03 ± 0.02	0.04 ± 0.04	0.03 ± 0.03	0.26 ± 0.30	0.32 ± 0.81
As	0.57 ± 0.45	1.9 ± 2.8	0.10 ± 0.06	0.81 ± 0.75	2.5 ± 1.9
Cd	0.17 ± 0.17	0.31 ± 0.40	0.27 ± 0.23	1.5 ± 2.0	3.1 ± 6.8
Cr	1.3 ± 1.2	2.5 ± 2.4	0.45 ± 0.50	5.7 ± 6.9	14.4 ± 25.0
Fe	395 ± 384	912 ± 775	182 ± 181	2544 ± 2578	5663 ± 8444
Mo	0.66 ± 0.49	0.43 ± 0.79	0.09 ± 0.13	0.61 ± 0.54	1.4 ± 1.4
Ni	1.7 ± 0.77	1.7 ± 1.2	0.82 ± 1.2	4.7 ± 3.7	11.4 ± 15.6
Pb	8.7 ± 10.7	22.2 ± 31.1	7.5 ± 8.9	95.7 ± 116	159 ± 295
Sn	0.48 ± 0.41	0.81 ± 0.76	0.12 ± 0.13	1.43 ± 1.86	1.61 ± 2.25
V	0.55 ± 0.59	1.4 ± 1.2	0.27 ± 0.26	6.3 ± 4.6	15.2 ± 25.5
Zn	66.7 ± 62.6	123 ± 164	35.9 ± 35.2	443 ± 671	991 ± 2000
Crustal elements (mg/kg dw) (Mean± Std.dev.)					
Al	118 ± 88.2	278 ± 141	59.9 ± 36.5	674 ± 385	2002 ± 1820
Ca	4907 ± 3031	8870 ± 4343	7958 ± 5073	8365 ± 4641	19075 ± 9859
K	11793 ± 3655	9481 ± 3304	3989 ± 1436	632 ± 236	3832 ± 2208
Mg	2789 ± 861	3381 ± 1188	1148 ± 204	691 ± 265	3224 ± 1188
Sr	12.5 ± 9.0	22.7 ± 22.0	17.2 ± 11.6	17.1 ± 8.9	44.2 ± 29.0

TABLE II
TRACE ELEMENT CONCENTRATIONS OF TREE COMPONENTS AND LEAF LITTER SAMPLES IN BACKGROUND SITES

Components	1-year needle	2-year needle	Branch	Bark	Leaf litter
BACKGROUND SITES					
Anthropogenic elements (mg/kg dw) (Mean± Std.dev.)					
Ag	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.03	0.02 ± 0.01	0.03 ± 0.02
As	0.18 ± 0.11	0.31 ± 0.17	0.07 ± 0.03	0.21 ± 0.12	0.36 ± 0.23
Cd	0.25 ± 0.13	0.33 ± 0.19	0.49 ± 0.29	0.37 ± 0.12	0.38 ± 0.11
Cr	0.31 ± 0.17	0.51 ± 0.18	0.14 ± 0.08	0.62 ± 0.26	0.59 ± 0.20
Fe	88.5 ± 40.3	165 ± 60.6	98.5 ± 47.5	502 ± 197	427 ± 146
Mo	0.35 ± 0.24	0.05 ± 0.02	0.02 ± 0.01	0.06 ± 0.02	0.10 ± 0.05
Ni	2.2 ± 1.2	1.2 ± 0.62	0.50 ± 0.51	2.0 ± 0.25	1.0 ± 0.36
Pb	0.73 ± 0.80	0.89 ± 0.30	0.74 ± 0.29	2.4 ± 1.0	2.3 ± 0.65
Sn	0.15 ± 0.12	0.13 ± 0.09	0.07 ± 0.13	0.05 ± 0.02	0.06 ± 0.01
V	0.17 ± 0.05	0.39 ± 0.18	0.19 ± 0.09	1.1 ± 0.45	0.81 ± 0.31
Zn	21.9 ± 4.1	33.3 ± 24.4	8.5 ± 6.5	9.5 ± 4.1	29.1 ± 6.5
Crustal elements (mg/kg dw) (Mean± Std.dev.)					
Al	97.3 ± 33.1	204 ± 69.8	145 ± 64.7	531 ± 107	472 ± 178
Ca	4311 ± 1889	10861 ± 6095	8047 ± 4695	5116 ± 1435	11874 ± 3119
K	9008 ± 2105	8845 ± 2337	2465 ± 820	460 ± 149	3106 ± 1403
Mg	2391 ± 666	2721 ± 900	1016 ± 318	453 ± 83.5	1848 ± 761
Sr	16.8 ± 9.9	36.1 ± 23.4	27.9 ± 18.7	11.6 ± 2.5	32.7 ± 10.0

Substantially higher concentrations in industrial sites indicated that these industries were the major sources of anthropogenic trace elements in the area. A similar observation was reported by El-Hasan *et al.* [3] that measured the lowest trace element concentrations in bark samples in rural and background areas while the highest concentrations were observed in an industrial area.

Spatial variations of trace elements in the study area are illustrated in Fig. 1 and Fig. 2 using the measured concentrations of selected anthropogenic elements (Zn and V) in leaf litter samples as examples. The highest Zn concentrations were measured at sites close to the steel plants (Fig. 1) whereas higher V concentrations were measured at sites close to refinery and petrochemical plants (Fig. 2). These observations are supported by recent studies [10], [13]. Steel plants with electric arc furnaces (EAFs), the slag piles of steel plants, fuel-oil burning in the refinery and in petrochemical plants, coal burning for residential heating and industrial purposes, natural gas-fired power plant, ship dismantling plants and traffic emissions are the anthropogenic sources in the study area [10]. It was shown that elements like Zn, Pb, and Cu are markers for steel plants with EAFs while V is a marker for fuel-oil combustion [10], [13], [14].

Fe is generally classified as a crustal element. The mean Fe concentrations in the present study ranged between (182-5663 mg/kg dry weight) in the industrial sites, 2.1-11 times higher than those in background sites. This implies that the Fe contamination in the study area could be regarded as anthropogenic and this could be attributed to the large emissions of iron-steel plants in this region.

Mulgrew and Williams [15] reported that coniferous trees reflect the pollution in an area over a long period of time. They have suggested the use of the tree bark for assessing air pollution since bark is exposed to air pollutants directly from the atmosphere. Concentrations of major and trace elements in plants depend on accumulation of dry and wet deposition on outer plant components like needles or bark. On the average, anthropogenic trace element concentrations in 2-year needles were ~2.0 times higher than 1-year needles as a result of longer exposure to polluted air. The highest and lowest elemental concentrations were observed in leaf litter and branch samples, respectively (Table I). Results of this study indicated that trace elements accumulated in tree components could be used to assess the spatial distribution of air pollution in an industrial region.

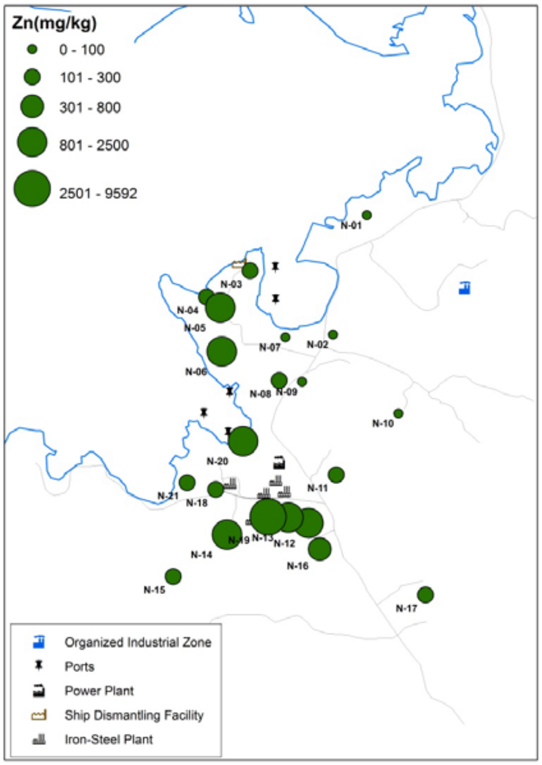

Fig.1 Spatial distribution of Zn concentration in Aliaga

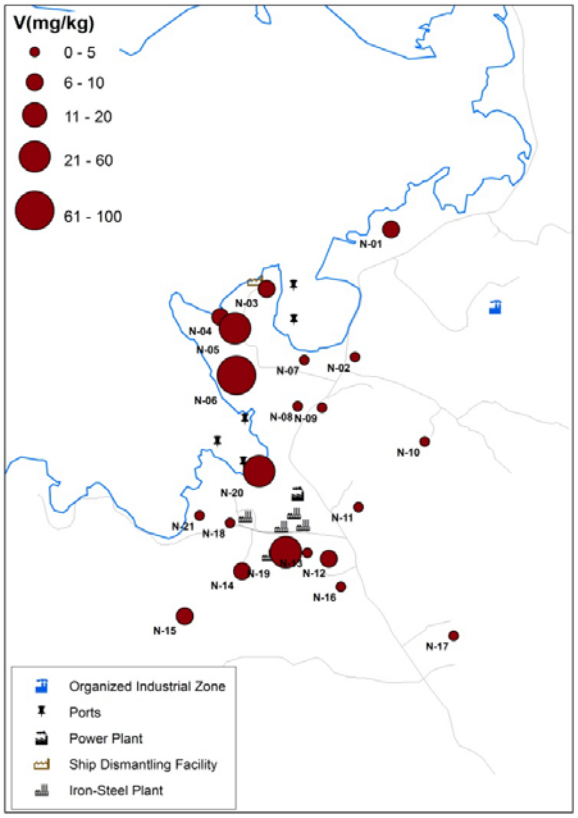

Fig.2 Spatial distribution of V concentration in Aliaga

The relationships between Zn and V measured in different samples were investigated by constructing correlation matrices (Table III). The statistically significant correlations ($p < 0.01$) between most of the tree components and leaf litter suggested that they are affected by air pollutants emitted from common sources in the area. These correlations further support the finding that trace elements measured in tree components could be used for biomonitoring of air pollution.

TABLE III
CORRELATION MATRICES FOR ZINC AND VANADIUM MEASURED IN DIFFERENT SAMPLES (SIGNIFICANT CORRELATIONS ARE SHOWN IN BOLD, $P < 001$)

Zn	1-Yr Needle	2-Yr Needle	Branch	Bark	Leaf litter
1-Yr Needle	1.00				
2-Yr Needle	**0.88**	1.00			
Branch	**0.73**	**0.57**	**1.00**		
Bark	**0.78**	**0.60**	**0.66**	1.00	
Leaf litter	**0.56**	**0.46**	0.37	**0.85**	1.00
V					
1-Yr Needle	**1.00**				
2-Yr Needle	**0.90**	**1.00**			
Branch	**0.66**	**0.72**	1.00		
Bark	**0.63**	**0.70**	0.53	**1.00**	
Leaf litter	**0.22**	**0.32**	0.16	**0.64**	1.00

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