

Instrumental neutron activation analysis of plant tissues and soils for biomonitoring in urban areas in Istanbul

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Abstract The aim of this study was to determine the elemental concentrations of plant tissues and soils collected in Istanbul to evaluate the possible use of selected tree species, *Carpinus betulus* L., *Quercus petraea* (Matuschka) Liebl., *Tilia argentea* Desf. ex DC., as biomonitors. The concentrations of 26 elements were determined by k_0 -INAA using Kayzero for Windows software. Generally, the element concentrations in samples from urban areas were found to be higher than those of control area. *Tilia argentea* Desf. ex DC. may be an effective biomonitor for As, Br, Ca, Cl, Cr, Fe, Hf, K, Sb, Sc, Sr, and Th.

Keywords k_0 -INAA · Biomonitor · Tree leaves · Tree twigs

Introduction

The rapid increase in population coupled with fast industrialization growth leads to serious environmental problems, including the production and release of toxic substances into the environment. Although metals are natural components of Earth's crust, the concentration of metals may reach toxic levels in many ecosystems due to the anthropogenic activities. Plants that are capable of

accumulating high concentrations of metals are identified as hyper accumulator plants and approximately 500 plant species have been reported as hyperaccumulator [1]. The accumulation of metals can vary among different plants growing in the same environment and the concentration of metals vary in the different part of plants such as roots, branches and leaves [2]. Metals can enter a plant either through the root system from the soil or from the atmospheric fallout on the surface of the plant tissues [3]. Hence, the determination of metal concentrations can be done in two ways: in washed or unwashed plant samples, depending on the purpose of the study. Analysis of unwashed and washed samples allows evaluating the deposition of metals over the plant surfaces to assess the degree of soilborne and airborne contamination. Various washing techniques such as washing with solvents, weak acid solutions were applied to leaves [4–6]. However, deionized water is used most often for washing leaves in the sample preparation step [7–10].

In recent years, many studies have been carried out in Turkey to study the possible use of various tree species as a possible biomonitor for metals [11–19]. However, only limited numbers of studies have been conducted in Istanbul in the last decade [20–22]. Since Istanbul is one of the most populous cities in the world, it suffers from environmental pollution similarly as other fast growing cities in the world, and an extensive survey of metal concentrations in Istanbul ecosystem may be beneficial. For this purpose, *Carpinus betulus* L. (European hornbeam), *Quercus petraea* (Matuschka) Liebl. (Sessile oak), and *Tilia argentea* DESF. ex DC. (Silver lime), which are some of the main tree species in Istanbul [23], were selected to study the element concentrations in the leaf and twig samples. The determination of element concentrations in *C. betulus* L., *T. argentea* DESF., *Q. pubescens* and *Q. rotundifolia* have been studied

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in different countries. The metal concentrations in *C. betulus* L., *T. argentea* DESF., and *Q. cerris* L. were investigated [24] and *T. argentea* DESF. was proposed as a good biomonitor. The element concentrations in leaves of oak species *Q. pubescens* and *Q. rotundifolia* were also investigated [25, 26]. The element contents of *Q. pubescens* leaves were not affected in the presence of soils with high concentrations of Cr, Mg, and Ni; however As was found to be the only element showing higher concentrations in leaves from areas with As-polluted soils. The *Q. rotundifolia* leaves accumulated higher content of As, Fe, and Mn than the other tree species investigated.

Various analytical methods, such as polarised X ray fluorescence spectrometer (EDPXRf), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma mass spectrometry (ICP-MS), ion chromatography with UV-Vis detection (IC-UV/Vis) were used for element determination in plant tissues and soils [27–32]. However, these methods require destruction of the matrix by chemicals, which may lead to contamination problems and/or analyte losses. Therefore, instrumental neutron activation analysis (INAA), a non-destructive method, appears superior for multi-elemental analysis of plant and soil samples [33–35].

The objectives of this study were: (1) to estimate the element concentrations in leaves, twigs and soils at selected areas in Istanbul by INAA; (2) to evaluate the element accumulation capability of *C. betulus* L., *Q. petraea* (Mattuschka) Liebl., and *T. argentea* DESF. ex DC. to test their possible use as biomonitors; (3) to evaluate the effect of washing by distilled water on the element concentrations in leaf and twig samples.

Experimental

Sampling and sample preparation

The study was conducted in Istanbul, the most crowded city of Turkey, with a population of about 15 million, providing 38 % of the total industrial output of Turkey and with a number of registered motor vehicles about 3.5 million. Therefore, the quality of the environment was affected by human activities, traffic and industrial production. Samples were collected during autumn 2014 from a relatively clean area, Atatürk Arboretum (S1, control area) and urban areas, Bahçeköy (S2), Levent (S3) and Yıldız Park (S4) (Fig. 1). In total, 22 samples including leaves and twigs of the tree species and 15 soil samples were collected. The numbers of leaves and twigs per species and soils per sampling area were as follows: *C. betulus* L. $n = 7$ (S1 = 2, S2 = 2, S4 = 3), *Q. petraea*

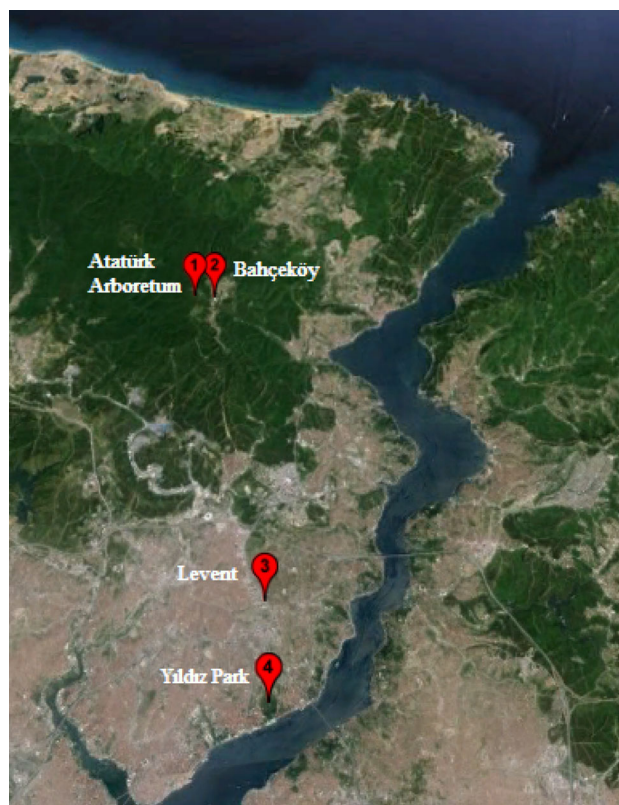


Fig. 1 The map of study area

(Mattuschka) Liebl. $n = 8$ (S1 = 2, S2 = 2, S4 = 4), *T. argentea* DESF. $n = 7$ (S1 = 2, S2 = 2, S3 = 3), and soil (S1 = 3, S2 = 3, S3 = 3, S4 = 6). Samples from the trees were collected from all 4 directions up to 2 m height to make one sample for analysis from each tree, whereas soil samples were taken from topsoil of 5 to 15 cm depth at each area.

Leaf and twig samples were divided into two sub-samples. First sub-sample was washed with distilled water, and then oven dried at 40 °C for 24 h to avoid the loss of volatile elements. The second sub-sample was untreated. Then, both washed and unwashed leaf samples were ground in a agate ball mill and twig samples were ground in a cryogenic mill at liquid nitrogen temperature. Samples were sieved through a 0.6 mm mesh to prepare well homogenized samples and about 150, 120 and 50 mg of the respective samples were packed into disc-shaped polyethylene (PE) capsules with a 25-mm diameter made by sealing of PE foils with 0.2 mm thickness.

Analysis

Element concentrations of samples were determined by k_0 method of instrumental neutron activation analysis (k_0 -INAA) using Kayzero for Windows software [36].

Irradiations were performed in the experimental nuclear reactor LVR-15 of the Research Center Řež, Ltd. within the CANAM infrastructure (MEYS project No. LM2011019). Short-time irradiation (1 min) in channel H1 and long-time irradiation (3 h) in channel H8 were carried out to determine elements forming short- and long-lived radionuclides, respectively. The neutron flux parameters were determined using Au + Mn + Rb and Au + Mo + Rb monitor sets for short- and long-time irradiations, respectively (Table 1).

Gamma-ray spectra were measured in loss-free counting mode using three coaxial HPGe detectors with the following parameters: PGT (used after short-time irradiation only): relative efficiency 20.3 %, FWHM 1.75 keV at 1332.5 keV, P/C 49.8:1, Canberra: relative efficiency 77.8 %, FWHM 1.87 keV at 1332.5 keV, P/C 82.5:1, Ortec: relative efficiency 52.9 %, FWHM 1.76 keV at 1332.5 keV, P/C 73.1:1. Decay times, measurement times and geometries were selected according to sample activities to determine as many elements as possible with a low uncertainty.

Statistical analyses of element concentrations in soils and plant tissues were carried out using one-way analysis of variance (ANOVA) and differences between the control and urban areas were considered to be significant at $p < 0.05$.

Standard reference materials (SRMs) NIST SRM 1547 Peach Leaves, NIST SRM 2711 Montana Soil and NIST SRM 1633b Constituent Elements in Coal Fly Ash were analysed for quality control purposes. The SRMs were irradiated together with samples in each irradiation batch. Agreement of element contents found in SRMs, x_{lab} , with certified values, x_{cert} , was tested with E_n number as defined in [37].

Results and discussion

Quality control analyses

Table 2 shows the results obtained for SRMs. It can be seen that for most of the elements, experimental values are in agreement with the NIST values ($E_n \leq 1$). However, discrepancies between the experimental and assigned values of Cr, Na, and Sb in NIST SRM 1547, and Sb in NIST

SRM 1633b were observed. Since the concentrations of the above-mentioned elements were in good agreement with NIST SRM 2711 values, no systematic cause can be seen. On the other hand, a problem may arise when comparing our results with the noncertified NIST values of Cr, Sb and Yb in NIST SRM 1547 and 1633b. The noncertified NIST values were also taken into account for calculation of E_n number using the approach described elsewhere [37]. Consequently, the results for SRMs suggested that the analytical procedure employed was adequate for determining element concentrations in plant and soil samples.

Results for soils

The concentrations of elements in soil samples are presented in Table 3. In general, the lowest element concentrations were determined in the control region (S1), whereas the highest element concentrations were found in urban areas, especially in S4. According to ANOVA test, Al, Eu, Fe, K, Na, Ni, Sc, and Zn concentrations in soils of all urban areas are significantly higher than those in S1 ($p < 0.05$). In the control area, only Cr and Hf concentrations were found to be the highest. Besides, the differences between means of these elements in the control and urban areas are only significant for S4. The concentration of Cl in S3 and Sr in S1 and S2 was found to be lower than detection limits. Element concentrations were compared with the World average soil values reported [2]. By this comparison, it can be seen that the concentrations of As, Co, Mn, and Ni in all urban areas, Br and Sc in S4, Ce and Hf in S2, Cr and Sb in all sampling areas, Rb in S2 and S4, and Zn in S3 and S4 are higher than the World average values. The concentrations of Al, Ca, Fe, K, and Na, which are the abundant elements in Earth’s crust, were compared with continental crust values compiled from [38]. It was found that the concentrations of these elements are lower than those in Earth’s crust.

By comparing the elemental concentrations in soils with the continental crust values, enrichment factors (EF) of elements were calculated using Eq. (1) [39].

$$EF = \frac{C_{xt}/C_{xr}}{C_{rt}/C_{rr}} \tag{1}$$

where C_{xt} and C_{xr} are the concentration of element x in the sampling area and Earth’s crust, C_{rt} and C_{rr} are the concentration of reference element in the sampling area and Earth’s crust, respectively. Iron was used as the reference element and element concentrations in Earth’s crust were taken from [2]. Five contamination categories, $EF < 2$: minimal enrichment, $2 \leq EF < 5$: moderate enrichment, $5 \leq EF < 20$: significant enrichment, $20 \leq EF < 40$: very high enrichment and $EF \geq 40$: extremely high enrichment, are recognized on the basis of the enrichment factor [40].

Table 1 Neutron flux parameters (mean \pm SD, $n = 10$)

Channel	H1	H8
α	0.038 \pm 0.029	0.006 \pm 0.012
f	24.84 \pm 0.42	35 \pm 6
F_c	369,000 \pm 16,000	350,000 \pm 70,000

Table 2 Results for reference materials

Element (mg kg ⁻¹) ^a	NIST SRM 1547				NIST SRM 2711				NIST SRM 1633b			
	$x_{\text{cer}} \pm u_{\text{cer}}$	$x_{\text{lab}} \pm u_{\text{lab}}$	LD	E_n	$x_{\text{cer}} \pm u_{\text{cer}}$	$x_{\text{lab}} \pm u_{\text{lab}}$	LD	E_n	$x_{\text{cer}} \pm u_{\text{cer}}$	$x_{\text{lab}} \pm u_{\text{lab}}$	LD	E_n
Al	249 ± 8	262 ± 19	3.1	0.63	6.53 ± 0.09 (%)	6.28 ± 0.44 (%)	0.017	0.56	15.05 ± 0.27 (%)	14.4 ± 1.0 (%)	0.018	0.63
As	0.060 ± 0.018	0.08 ± 0.021	0.06	0.72	105 ± 8	103 ± 7	0.7	0.19	136.2 ± 2.6	132 ± 9	0.8	0.45
Ba	1.24 ± 4	1.30 ± 13	7	0.44	726 ± 38	710 ± 60	1.4	0.23	709 ± 27	700 ± 90	1.2	0.10
Br	(11) ^b	10.5 ± 0.7	0.07	0.38	(5)	5.0 ± 0.5	0.8	0.00	(2.9)	2.8 ± 0.5	0.9	0.13
Ca (%)	1.56 ± 0.02	1.60 ± 0.12	0.017	0.33	2.88 ± 0.08	2.72 ± 0.20	0.06	0.74	1.51 ± 0.06	1.42 ± 0.12	0.042	0.67
Ce	(10)	10.6 ± 0.8	0.14	0.47	(69)	75 ± 5	0.34	0.70	(190)	190 ± 14	0.34	0.00
Cl	360 ± 19	351 ± 27	7	0.27	NR		70	NR		50		
Co	(0.07)	0.072 ± 0.008	0.009	0.19	(10)	9.6 ± 0.7	0.10	0.04	(50)	47.9 ± 3.4	0.11	0.35
Cr	(1)	1.35 ± 0.13	0.18	2.13	(47)	45.5 ± 3.3	1.5	0.26	198.2 ± 4.7	197 ± 14	2.5	0.08
Cs	NR ^c		0.014		(6.1)	6.6 ± 0.5	0.14	0.60	(11)	10.7 ± 0.8	0.27	0.22
Eu	(0.17)	0.179 ± 0.019	0.0031	0.35	(1.1)	1.14 ± 0.16	0.021	0.03	(4.1)	4.15 ± 0.44	0.036	0.08
Fe	218 ± 14	206 ± 16	8	0.56	2.89 ± 0.06 (%)	2.78 ± 0.20 (%)	0.008	0.53	7.78 ± 0.23 (%)	7.5 ± 0.5 (%)	0.013	0.51
Hf	NR		0.013		(7.3)	7.7 ± 0.7	0.11	0.05	(6.8)	6.8 ± 0.7	0.20	0.00
K (%)	2.43 ± 0.03	2.35 ± 0.18	0.0036	0.44	2.45 ± 0.08	2.35 ± 0.23	0.13	0.41	1.95 ± 0.03	1.86 ± 0.21	0.13	0.42
La	(9)	8.8 ± 0.6	0.012	0.18	(40)	35.6 ± 2.5	0.13	0.93	(94)	83 ± 6	0.13	0.99
Mn	98 ± 3	99 ± 7	0.10	0.13	638 ± 28	625 ± 44	0.8	0.25	131.8 ± 1.7	130 ± 9	1.0	0.20
Na	24 ± 2	40.9 ± 3.0	0.25	4.69	1.14 ± 0.03 (%)	1.16 ± 0.09 (%)	0.0008	0.21	0.201 ± 0.003 (%)	0.197 ± 0.015 (%)	0.0008	0.26
Ni	0.69 ± 0.09		70		20.6 ± 1.1	31 ± 12	19	0.86	120.6 ± 1.8	136 ± 25	32	0.61
Rb	19.7 ± 1.2	18.0 ± 1.4	0.5	0.76	(110)	114 ± 9	6	0.28	(140)	141 ± 12	11	0.05
Sb	(0.02)	0.034 ± 0.006	0.016	2.21	19.4 ± 1.8	18.6 ± 1.3	0.13	0.36	(6)	4.91 ± 0.40	0.18	1.51
Sc	(0.04)	0.044 ± 0.0035	0.0009	0.75	(9)	9.3 ± 0.7	0.0041	0.26	(41)	40.5 ± 2.9	0.008	0.10
Sm	(1)	1.00 ± 0.08	0.0030	0.00	(5.9)	5.63 ± 0.43	0.039	0.37	20 ± 2	17.6 ± 1.3	0.047	1.00
Sr	53 ± 4	55 ± 6	7	0.28	245.3 ± 0.7	245 ± 41	70	0.01	1 041 ± 18	990 ± 110	120	0.46
Tb	(0.1)	0.104 ± 0.008	0.007	0.31	NR		0.06		(2.6)	2.59 ± 0.19	0.10	0.03
Th	(0.05)	0.055 ± 0.008	0.014	0.53	(14)	13.4 ± 0.9	0.12	0.36	25.7 ± 1.3	24.6 ± 1.8	0.20	0.50
Zn	17.9 ± 0.4	19.1 ± 1.4	0.37	0.82	350.4 ± 4.8	340 ± 31	2.2	0.33	(210)	206 ± 20	3.7	0.14

^a Unless otherwise given^b Noncertified value^c NR: element value is not reported in the certificate

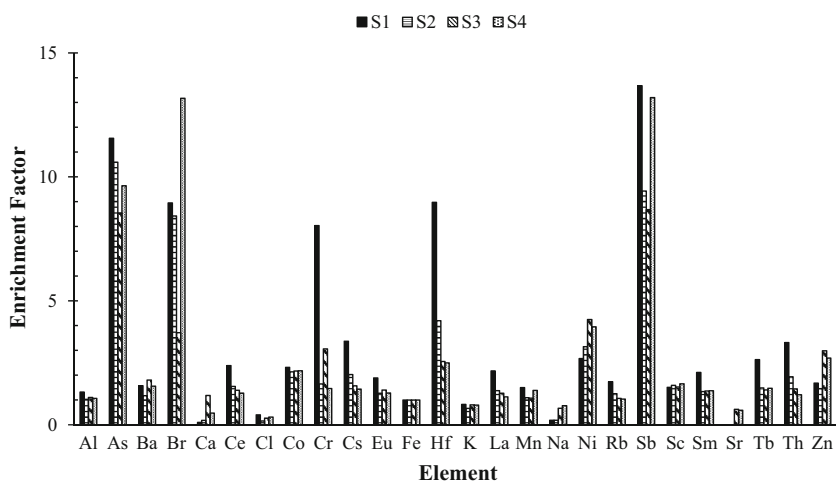
Table 3 Concentrations of elements (mg kg⁻¹ dry mass) in soils (mean ± SD)

Element	S1 (n = 3)	S2 (n = 3)	S3 (n = 3)	S4 (n = 6)	World soil average [2]
Al (%)	3.31 ± 0.29	5.44 ± 0.24*	5.7 ± 0.5*	5.9 ± 0.5*	8.08**
As	6.4 ± 1.7	12.3 ± 1.7*	9.7 ± 2.2	11.7 ± 2.4*	6.83
Ba	193 ± 11	304 ± 35*	450 ± 200	421 ± 38*	460
Br	5.5 ± 1.0	10.9 ± 2.1*	4.7 ± 2.9	18 ± 7*	10
Ca (%)	0.11 ± 0.10	0.43 ± 0.22	2.7 ± 1.1*	1.17 ± 0.40*	3.85**
Ce	44 ± 11	60 ± 14	52 ± 6	51.7 ± 3.4	56.7
Cl	79 ± 15	65.5 ± 3.5	<44	135 ± 18*	300
Co	7.1 ± 3.4	13.8 ± 4.6	13.6 ± 3.3	14.7 ± 2.0*	11.3
Cr	250 ± 100	106 ± 24	190 ± 170	98.8 ± 3.7*	59.5
Cs	3.09 ± 0.28	3.9 ± 0.8	3.0 ± 0.6	2.9 ± 1.8	5.06
Eu	0.69 ± 0.12	0.987 ± 0.038*	1.06 ± 0.16*	1.04 ± 0.07*	1.4
Fe (%)	1.38 ± 0.24	2.90 ± 0.26*	2.8 ± 0.7*	3.0 ± 0.6*	4.72**
Hf	8.2 ± 1.9	8.1 ± 1.7	4.8 ± 1.6	5.1 ± 1.2*	6.4
K (%)	0.65 ± 0.06	1.12 ± 0.12*	1.32 ± 0.29*	1.40 ± 0.12*	1.98**
La	19.9 ± 3.6	27 ± 5	23.9 ± 4.4	22.9 ± 2.7	27
Mn	410 ± 220	630 ± 290	610 ± 140	840 ± 140*	488
Na (%)	0.160 ± 0.022	0.34 ± 0.07*	1.20 ± 0.21*	1.48 ± 0.26*	2.50**
Ni	16.3 ± 2.3	40.7 ± 3.8*	53 ± 14*	53 ± 12*	29
Rb	48 ± 8	73 ± 6*	60 ± 5	63 ± 7*	68
Sb	0.84 ± 0.20	1.217 ± 0.021*	1.09 ± 0.18	1.78 ± 0.24*	0.67
Sc	5.1 ± 0.7	11.3 ± 1.0*	10.5 ± 2.4*	12.3 ± 2.3*	11.7
Sm	3.0 ± 0.6	4.1 ± 0.7	4.0 ± 0.5	4.4 ± 0.6*	4.6
Sr	<41	<70	146 ± 35	148 ± 23	175
Tb	0.48 ± 0.19	0.58 ± 0.08	0.53 ± 0.10	0.60 ± 0.08	0.63
Th	7.3 ± 1.6	9.0 ± 2.0	6.6 ± 0.8	5.9 ± 0.6	9.2
Zn	36 ± 13	65.7 ± 1.4*	131 ± 16*	127 ± 37*	70

* Significant difference in means of control area and urban area, *p* < 0.05

** Continental crust values

Fig. 2 Enrichment factors of elements in soils



The EFs of elements in soils are given in Fig. 2. It can be seen that As and Sb are significantly enriched in soils in all sampling areas, and Br is also significantly enriched in all sampling areas except for S3. In S1, Cr and Hf were also

found to be significantly enriched. Co and Ni are moderately enriched in soils in all sampling areas. Hf and Zn are also moderately enriched in urban areas. Elements with EF values that are considerably higher than 1, can be

considered not originating from the local soil background and may be attributed to anthropogenic sources such as traffic and industrial activities. However, results obtained from this study may need a more detailed investigation to clarify the reason of high enrichment factors.

The difference between element concentrations in washed and unwashed plant tissues was evaluated prior to data analysis. The correlation between mean element concentrations for unwashed and washed leaf and twig samples are shown in Fig. 3. Positive correlations (~ 0.99) were found between element concentrations in unwashed and washed samples in all areas, which suggests no influence of the washing procedure for both leaf and twig samples. Therefore, in further data evaluation, only the results from unwashed samples were used.

The mean concentrations of elements in unwashed leaf samples of *C. betulus* L., *Q. petraea* (Mattuschka) Liebl., and *T. argentea* DESF. ex DC. are presented in Table 4. Element concentrations of leaf samples were compared with the excessive or toxic concentrations in mature leaf tissue generalized for various species by Kabata-Pendias [2].

In *C. betulus* L. leaves, Al, Cl, Cr, Cs, Fe, Hf, Sb, Sc, Sr, Th, and Zn concentrations in S4 were significantly higher than those in S1 according to ANOVA test ($p < 0.05$). However, Mn, Ni and Rb concentrations in S1 are significantly higher than those in S4. No significant statistical differences were found between the means of element concentrations in S1 and S2 except for Mn, the concentration of which is higher in the S1.

In *Q. petraea* (Mattuschka) Liebl. leaves, ANOVA test showed that As, Fe, La, Sb, Sm, and Tb concentrations in S2 and Ce, Cs, and Zn concentrations in S4 were significantly higher than those in the control area ($p < 0.05$). Mn concentration in the control area is significantly higher than those in S2. The difference between the means of Mn concentrations in control area and S4 was insignificant due to the high standard deviation of Mn concentration determined in S4.

In *T. argentea* DESF. ex DC. leaves, Cr, Hf, K, Sb, and Zn concentrations in S2, Cr, Fe, and Hf concentrations in S3 were significantly higher than those in the control area according to ANOVA test ($p < 0.05$). On the other hand,

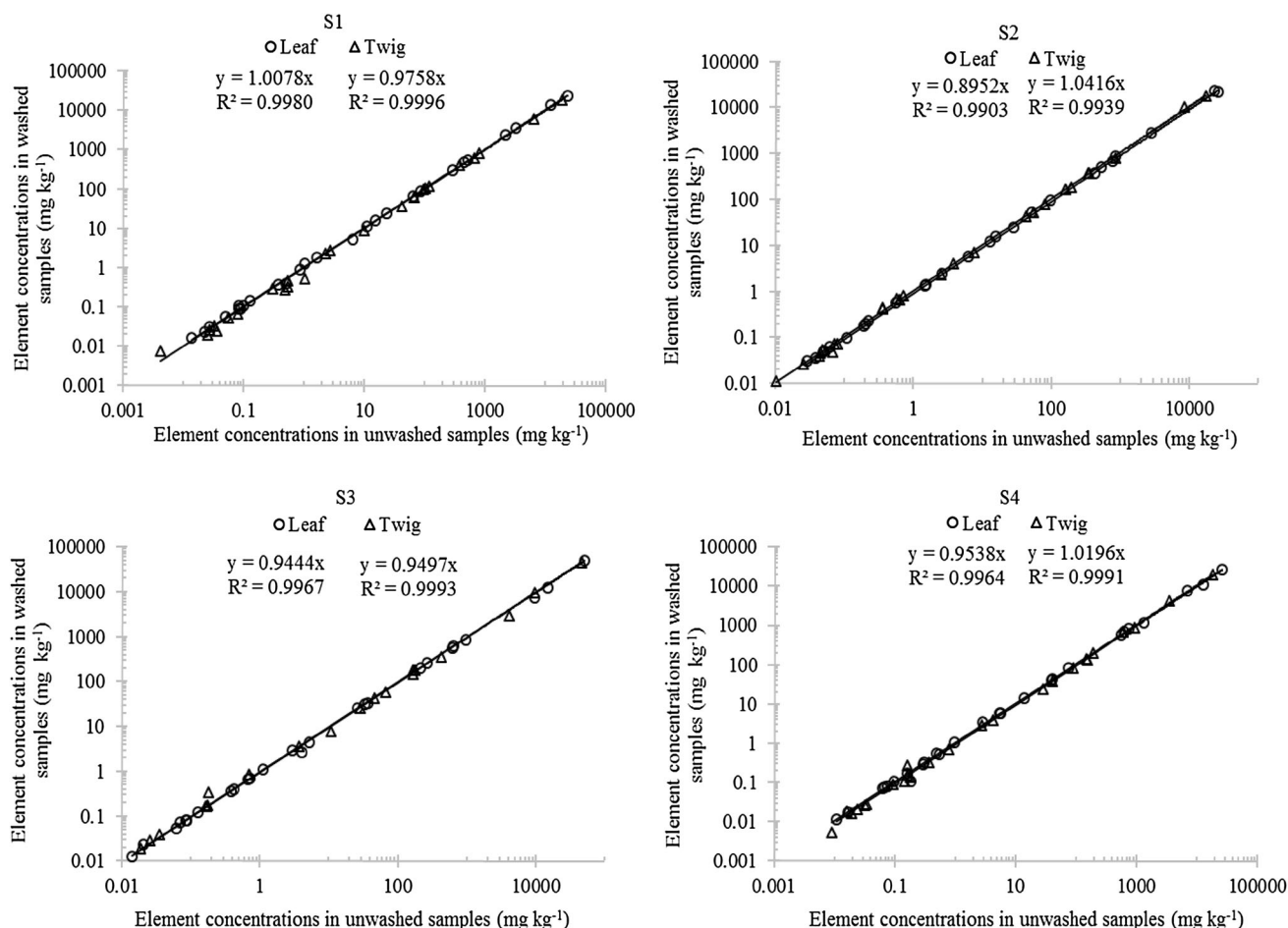


Fig. 3 Correlation between element concentrations in unwashed and washed leaf and twig samples in sampling areas

Table 4 Concentrations of elements (mg kg⁻¹ dry mass) in leaf samples (mean ± uncertainty, k = 2)

Element	<i>Carpinus betulus</i> L.			<i>Quercus petraea</i> (Mattuschka) Liebl.			<i>Tilia argentea</i> DESF. ex DC.			Excessive or toxic [2]
	S1 (n = 2)	S2 (n = 2)	S4 (n = 3)	S1 (n = 2)	S2 (n = 2)	S4 (n = 4)	S1 (n = 2)	S2 (n = 2)	S3 (n = 3)	
Al	560 ± 70	472 ± 37	940 ± 70*	341 ± 39	515 ± 41	544 ± 43	503 ± 38	623 ± 45	625 ± 46	
As	0.122 ± 0.020	0.136 ± 0.020	0.380 ± 0.040	0.112 ± 0.022	0.191 ± 0.026*	0.207 ± 0.026	0.179 ± 0.029	0.248 ± 0.032	0.42 ± 0.05	5–20
Ba	83 ± 6	53.0 ± 4.2	40.4 ± 3.8	103 ± 8	202 ± 15	133 ± 10	46.1 ± 4.0	38.8 ± 3.7	33.4 ± 3.5	500
Br	9.1 ± 0.6	10.3 ± 0.7	17.7 ± 1.2	8.7 ± 0.6	10.9 ± 0.8	9.0 ± 0.7	17.1 ± 1.2	25.8 ± 1.8	37.4 ± 2.6	
Ca (%)	1.54 ± 0.12	1.65 ± 0.14	2.25 ± 0.19	1.52 ± 0.12	2.07 ± 0.18	3.61 ± 0.27	5.01 ± 0.37	3.19 ± 0.23	5.15 ± 0.38	
Ce	1.59 ± 0.13	2.45 ± 0.20	1.21 ± 0.11	1.82 ± 0.15	2.87 ± 0.22	0.81 ± 0.10*	2.30 ± 0.18	2.49 ± 0.20	1.13 ± 0.11	
Cl (%)	0.314 ± 0.024	0.315 ± 0.023	1.10 ± 0.08*	0.193 ± 0.014	0.131 ± 0.010	0.257 ± 0.020	0.575 ± 0.042	0.417 ± 0.031	0.98 ± 0.07	
Co	0.437 ± 0.031	0.669 ± 0.049	0.391 ± 0.028	0.333 ± 0.024	0.73 ± 0.05	0.232 ± 0.017	0.495 ± 0.036	0.293 ± 0.022	0.386 ± 0.028	15–50
Cr	1.03 ± 0.11	1.06 ± 0.11	3.52 ± 0.27*	0.92 ± 0.14	1.40 ± 0.18	2.17 ± 0.18	1.24 ± 0.13	2.11 ± 0.18*	2.99 ± 0.24*	5–30
Cs	0.058 ± 0.006	0.035 ± 0.006	0.073 ± 0.008*	0.135 ± 0.011	0.063 ± 0.008	0.051 ± 0.006*	0.105 ± 0.009	0.052 ± 0.007*	0.062 ± 0.007	
Eu	0.0158 ± 0.0014	0.0417 ± 0.0031	0.0194 ± 0.0017	0.0305 ± 0.0024	0.088 ± 0.009	0.0179 ± 0.0015	0.030 ± 0.007	0.0255 ± 0.0020	0.0208 ± 0.0019	
Fe	261 ± 19	272 ± 20	750 ± 50*	246 ± 18	413 ± 30*	492 ± 34	386 ± 28	582 ± 41	646 ± 46*	
Hf	0.026 ± 0.008	0.020 ± 0.005	0.088 ± 0.009*	0.027 ± 0.006	0.028 ± 0.005	0.047 ± 0.007	0.037 ± 0.006	0.070 ± 0.008*	0.071 ± 0.008*	
K (%)	1.22 ± 0.09	1.18 ± 0.09	1.20 ± 0.09	1.13 ± 0.08	1.98 ± 0.14	1.30 ± 0.10	1.51 ± 0.11	4.66 ± 0.37*	1.51 ± 0.11	
La	0.77 ± 0.06	1.60 ± 0.11	0.669 ± 0.047	0.77 ± 0.06	1.31 ± 0.10*	0.497 ± 0.035	1.54 ± 0.11	1.52 ± 0.11	0.69 ± 0.05*	
Mn (%)	0.384 ± 0.027	0.097 ± 0.007*	0.0555 ± 0.0039*	0.193 ± 0.014	0.124 ± 0.009*	0.104 ± 0.007	0.0598 ± 0.0043	0.0402 ± 0.0228	0.0272 ± 0.0019	0.04–0.10
Na (%)	0.0411 ± 0.0029	0.0443 ± 0.0032	0.155 ± 0.011	0.078 ± 0.005	0.099 ± 0.008	0.100 ± 0.007	0.0554 ± 0.0039	0.093 ± 0.007	0.099 ± 0.007	
Ni	8.1 ± 1.1	4.9 ± 1.1	4.1 ± 1.2*	8.3 ± 1.1	10.1 ± 1.4	6.9 ± 1.2	6.5 ± 1.1	3.8 ± 1.1	4.1 ± 1.2	10–100
Rb	17.1 ± 1.4	8.8 ± 0.7	3.81 ± 0.42*	16.2 ± 1.3	17.8 ± 1.4	7.8 ± 0.6	16.3 ± 1.5	12.6 ± 1.1	5.3 ± 0.5*	
Sb	0.069 ± 0.009	0.143 ± 0.011	0.592 ± 0.042*	0.058 ± 0.007	0.155 ± 0.012*	0.356 ± 0.025	0.135 ± 0.012	0.320 ± 0.023*	0.74 ± 0.06	150
Sc	0.076 ± 0.006	0.077 ± 0.006	0.204 ± 0.015*	0.075 ± 0.005	0.111 ± 0.008	0.113 ± 0.008	0.105 ± 0.008	0.138 ± 0.010	0.130 ± 0.009	
Sm	0.070 ± 0.005	0.191 ± 0.014	0.092 ± 0.007	0.133 ± 0.009	0.361 ± 0.025*	0.078 ± 0.006	0.132 ± 0.010	0.120 ± 0.009	0.087 ± 0.006	
Sr	44.5 ± 4.9	42 ± 6	86 ± 8*	30.5 ± 4.6	29.0 ± 3.5	79 ± 9	144 ± 11	86 ± 10	217 ± 16	
Tb	0.0114 ± 0.0021	0.0260 ± 0.0028	0.0119 ± 0.0026	0.0175 ± 0.0024	0.0484 ± 0.0040*	0.0124 ± 0.0024	0.0147 ± 0.0024	0.0139 ± 0.0024	0.0143 ± 0.0027	
Th	0.049 ± 0.007	0.042 ± 0.007	0.125 ± 0.012*	0.045 ± 0.007	0.055 ± 0.008	0.068 ± 0.009	0.067 ± 0.008	0.088 ± 0.010	0.085 ± 0.010	
Zn	28.2 ± 2.0	29.3 ± 2.1	41.6 ± 2.9*	22.5 ± 1.6	23.1 ± 1.8	35.6 ± 2.6*	17.7 ± 1.3	32.2 ± 2.3*	26.5 ± 1.9	100–400

* Significant difference of means for control area and urban areas, p < 0.05

Cs concentration determined in S1 is significantly higher than in S2, and La and Rb concentrations than those in S3.

Our results showed that the element concentrations in samples from urban areas, particularly in *C. betulus* L. in S4, are higher than those of control area. As S4 is located at the centre of the city, intense traffic may cause metal contamination. In addition, when compared to *C. betulus* L. and *Q. petraea* (Mattuschka) Liebl. in the same sampling area, *T. argentea* DESF. ex DC. leaves contain higher As, Br, Ca, Cl, Cr, Fe, Hf, K, Sb, Sc, Sr, and Th concentrations.

The determined concentrations of the elements Ag, As, Ba, Co, Cr, Ni, Sb, and Zn are below the toxic concentration range in leaves, which have been specified by Kabata-Pendias [2]. However, Mn concentrations were found to be in the toxic range, or even higher, except for the leaves of *T. argentea* DESF. ex DC. in S3.

Figure 4 shows the ratio of element concentrations in leaves to twigs. For elements, whose concentrations were below the detection limits in twigs, the ratios were not calculated. The results show that most of the elements are more accumulated in leaves than in twigs in all tree species. However, the ratio was found to be less than 1, in the range of 0.7–0.9, for Ba in *C. betulus* L. and in *T. argentea* DESF. ex DC. in S1 and in S2; for Co in *C. betulus* L. in control area and in *Q. petraea* (Mattuschka) Liebl. in S2, for La in *Q. petraea* (Mattuschka) Liebl. in S1, and for Sr in *C. betulus* L. in all areas and in *Q. petraea* (Mattuschka) Liebl. in S1 and in S2. On the other hand, it should be emphasized that the leaf to twig ratio of Zn is also less than 1 for all tree species in S1, S2 and S3, and is equal to 1 for all tree species in S4. Therefore, it can be said that Zn is more accumulated in twigs than in leaves for the investigated tree species in this study.

Conclusions

In this study, the element concentrations of the leaf and twig samples of *C. betulus* L. (European hornbeam), *Q. petraea* (Mattuschka) Liebl. (Sessile oak), and *T. argentea* Desf. ex DC. (Silver lime) and top soils from control and urban areas in Istanbul were determined by INAA for biomonitoring purposes. In a big city like Istanbul, it is not possible to separate clean area and urban areas with exact borders. Therefore, some of the results obtained from the control area and urban areas showed similarities. When interpreting the results of this study, one should take into consideration that the samples were collected in a short period of time in autumn 2014, and only top-soils were taken. However, there are also many other biotic, abiotic and seasonal factors that affect elemental accumulation by the plant. In leaf and twig samples, the correlation values showed that the washing

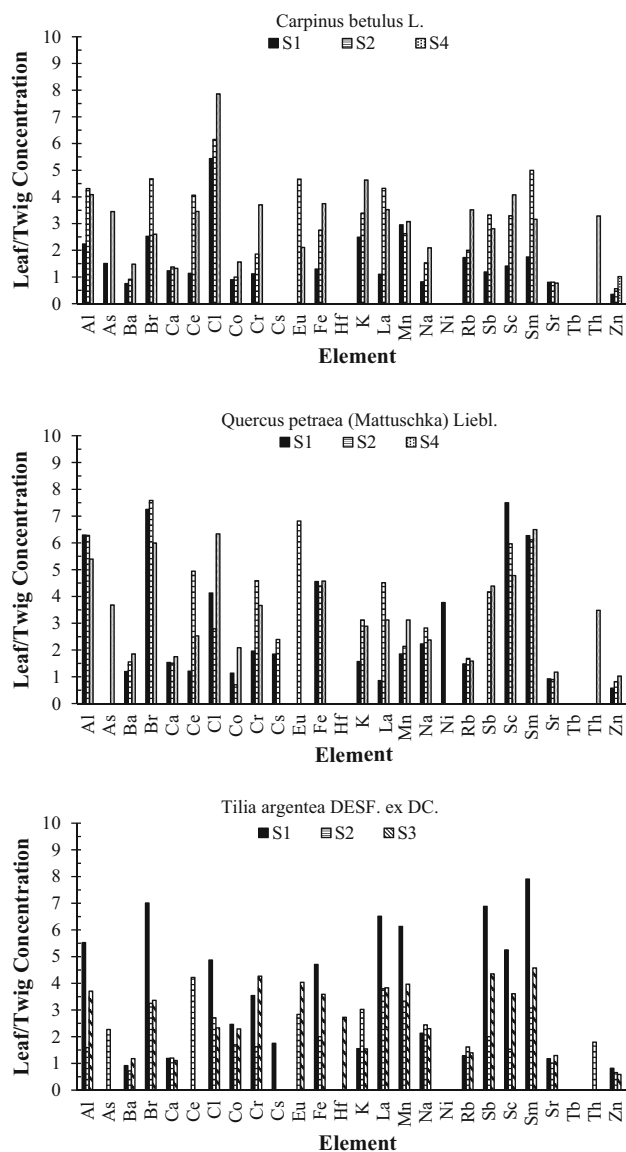


Fig. 4 Comparison of element concentrations in leaf and twig samples

process did not affect element concentrations in the samples analyzed. It can be said that the element contents of plant samples originated either by uptake from soil or the fallout elements may have been absorbed by plant tissues during growth of the plant. In general, the lowest element concentrations were determined in Atatürk Arboretum (control area) and the highest element concentrations were determined in urban areas. The levels of element concentrations in the leaves of all tree species are generally similar and all species could be combined for biomonitoring purposes in urban areas. Nevertheless, it can be emphasised that among the tree species analysed, *Tilia argentea* Desf. ex DC. can be considered as the most effective biomonitor, especially for the elements As, Br, Ca, Cl, Cr, Fe, Hf, K, Sb, Sc, Sr, and Th.

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