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ORIGINAL PAPER

ASSESSMENT OF THE PHYTOEXTRACTION POTENTIAL OF THIRTEEN PLANT SPECIES FOR CHROMIUM AND VANADIUM AND THEIR RELATIONSHIP WITH SULFUR AND HISTIDINE

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Abstract

The aim of this study has been to examine the phytoextraction potential of thirteen plant species for chromium (Cr) and vanadium (V) and their relationship with sulfur and histidine. The species including *Juglans regia* L., *Platanus* L., *Pinus nigra* L., *Thuja (Cupressaceae), Salix matsudana, Cupressus arizonica, Eleagnus ang., Vitis vinifera, Nerium olean., Robinia pse., Populous nigra, Grasses and Cedrus libani* were collected from two highly industrialized cities: Bursa and Gaziantep, in Turkey. The determinations were carried out by the ICP-MS and HPLC-MS methods. Concentrations of chromium and vanadium were in the ranges of 198-10 484 and 40-1100 μg kg^{-1}, respectively. Concentrations of sulfur were in the range of 705-8762 mg kg^{-1}, while the concentrations of histidine were found to be between 1 and 33 mg kg^{-1}. The ratios of the highest to the lowest chromium concentrations for *Salix, Nerium olean. and Thuja (Cupressaceae)* were found to be 16.4, 12 and 12.9-fold, respectively. Similarly, the ratios of the highest to the lowest vanadium concentrations for plant species are 2.9-fold for *Thuja*, 4.1-fold for *Pinus nigra*, 5.9-fold for *Vitis vin.* and 3.5-fold for *Robinia pseu.* Thus, the plant species mentioned above may be considered as a biomonitor and/or having the hyperaccumulator potential for chromium and vanadium. This is the first study in the literature to explore the relationship between the concentrations of histidine and sulfur with chromium and vanadium for the analyzed plant samples. It can be concluded that increased chromium concentrations in *Salix* leaves stimulate sulfur related with amino acids in this plant.

Keywords: chromium, vanadium, sulfur, trees, ICP-MS.

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INTRODUCTION

Environmental pollution with various forms of chromium results from its numerous uses in the chemical industry, production of dyes, wood preservation, leather tanning, chrome plating, manufacturing of various alloys, and many other applications and products (Zhitkovich 2011). Chromium is a nonessential element for plants, unlike for humans and animals, and it induces toxicity in many plant species. Some toxic effects of high chromium concentrations in plants can be mentioned as a reduction in root growth and biomass, chlorosis, photosynthetic impairment, and finally plant death. Due to the common use of chromium and its toxicity, there is great interest in the determination of this element in environmental and biological matrices (Avci et al. 2013, Karaaslan, Yaman 2013). Hexavalent chromium compounds are well-established human respiratory carcinogens (Costa, Klein 2006). Hexavalent chromium (Cr(VI)) is one of the few carcinogenic metals that can directly react with the DNA and induce mutations (Chervona et al. 2012). Chromium and vanadium are redox-active heavy metals, while iron, copper, and cobalt enable redox reactions in the cell (Yaman 2006). Because many metals emitted into the environment, including chromium and vanadium, are toxic and, unlike organic compounds, they are non-biodegradable, the removal of excess metal ions from polluted sites is reasonably important. Biomonitoring can be defined as the use of organisms or biomaterials to obtain information on certain elements and/or compounds in the environment. The use of biomonitor plants makes it also possible to identify the sources of emissions and verify the overland transportation of heavy metals. Phytoextraction is a remarkable process, where heavy metals can be absorbed from the soil and accumulated into plants at high concentrations without the use of expensive equipment (Sheoran et al. 2016). The plants which possess the highest absorption abilities are called "hyperaccumulators" and are the most suitable ones for the phytoextraction of heavy metals. Several studies concluded that phytoextraction of heavy metals can be a feasible technology for decontamination of metal-contaminated soils (Sheoran et al. 2011, Akkus, Yaman 2016*a*,*b*,*c*,*d*). Furthermore, the use of hyperaccumulator plants can also prove to be valuable in cropping precious metals such as gold, platinum, thallium and nickel, which may be recovered by phytomining for commercial gain (Sheoran et al. 2009). All these procedures, i.e. biomonitoring, phytoextraction, phytoremediation and biomining, are based on the hyperaccumulation of certain chemical species by plants. Physiological studies have given a lead to gaining the basic understanding of metal hyperaccumulation mechanisms, including enhanced metal uptake, increased xylem loading and increased detoxification in the shoot (Verbruggen et al. 2009). It is understood that plant ligands play a role in the sequestration of metals from soils, transport to the aerial plant organ tissues and finally storage. Among them, nitrogen-donor ligands, and especially free amino acids, are assumed to play

a role in hyperaccumulators. Heavy metals are intracellularly chelated through the synthesis of amino acids, organic acids or heavy metal-binding ligands such as metallothioneins, phytochelatins, and subject to compartmentation within vacuoles. Of free amino acids, histidine can act as a tridentate ligand via its carboxylato, amine and imadazole functions, and therefore it is considered to be the most important compound for metal hyperaccumulation (Haydon, Cobbett 2007, Callahan et al. 2006, Hall 2002, Krämer et al. 1996). Furthermore, heavy metals have a strong impact on the metabolism of sulfur, which plays an essential role in metal detoxification, and the modulation of proteins involved in sulfur metabolism has been observed using proteomic approaches in several different hyperaccumulators (Dalcorso et al. 2013). In the literature, several plants have been reported as vanadium accumulators, such as Astragalus, Castillejo and Chrysothamnus (Reimann et al. 2001).

Briefly, the search for plant species which would perform the role of hyperaccumulators of heavy metals in industrialized regions and an attempt to explain detoxification mechanisms are important and interesting. A particularly interesting process in the detoxification and hyperaccumulation of heavy metals is the chelation of these elements. Histidine plays an important role in this process due to the presence of an imidazole ring. Another group of compounds forming complexes with numerous heavy metals in higher plants is composed of sulfur compounds, especially the phytochelatin precursor glutathione and cysteine rich proteins. Therefore, it was reasonable to undertake research into the quantitative relationship between heavy metals (chromium and vanadium) and the content of histidine and sulfur.

The aim of this study was not only to examine the relationship between chromium and vanadium with histidine and sulfur in leaves of 13 plants, but also to consider the degree of metal pollution in two industrialized cities in Turkey because the areas studied comprise industrial zones containing lead battery production, cement factory and other industrial plants. For the determinations, HPLC-MS and ICP-MS were used.

MATERIAL AND METHODS

Apparatus and reagents

Determinations of chromium, vanadium and sulfur were done by using a Perkin-Elmer SCIEX ELAN 9000 inductively coupled plasma mass spectrometer (ICP-MS) (PerkinElmer SCIEX, Concord, ON, Canada). Operation conditions for ICP-MS were taken from the manufacturer (PerkinElmer SCIEX 9000, Canada) (plasma gas flow rate: 15 dm^3 min^{-1}, carrier gas flow rate: 0.9 dm^3 min^{-1} and sample uptake rate: 1.0 dm^3 min^{-1}). A microwave digestion system (CEM MARSXpress) was used to digest the samples before

the analysis. Ultrapure water obtained from a water purification system (Millipore Direct-Q, Millipore Corporation, Bedford, MA, USA) was used for all samples and preparations of standard solutions. An Agilent 1200 HPLC-MS system was used for the determination of histidine. The selected ion monitoring (156 and 110 m/z) and scan mode equipped with positive ion electrospray ionization were used. Concentrated nitric acid (65%, Merck) was used in the digestion procedure. The element solutions were prepared by dilution of their stock solutions (1,000 mg dm^{3-}, Merck, Darmstadt, Germany).

Sampling and digestion

Plant leaves, including: *Juglans regia* L., *Platanus* L., *Pinus nigra* L, *Thuja (Cupressaceae), Salix matsudana, Cupressus arizonica, Eleagnus angus., Vitis vin., Nerium olean., Robinia pse. Populous nigra, Grasses* and *Cedrus libani* were collected around Gaziantep and Bursa cities of 1,500,000 and 2,000,000 population, respectively, in SE and NW Turkey (Figure 1). These plant species were selected because some of them had been reported as potential bioaccumulators for certain metals (Kaya, Yaman 2008*a*,*b*, 2010*a*,*b*, 2012*a*,*b*). Representative locations were chosen as sampling points in the surroundings of the industrial zones, comprising lead battery production, cement factory and other industrial plants, located around Gaziantep and Bursa, Turkey. The control samples were taken away from urban and industrial areas. Sampling was conducted in the summer of 2011. Batches of healthy, fresh plant leaves about 100 g in weight were taken from each site. Plant samples were transported in plastic bags to a laboratory, washed with tap water, and then rinsed with ultrapure water. The preparation and digestion of plant leaves in a microwave (MW) oven were detailed elsewhere (Akkus, Yaman 2016*a*,*b*,*c*). After addition 20 mL of 0.10 M nitric acid, the solution was filtered, if necessary, and the clear solution was analyzed by ICP-MS. Each sample was analyzed in triplicate and mean values were used as a result.

Statistically, one-way analysis of variance (ANOVA) was conducted to test the equality of mean values for each plant species. One of the pairwise comparison tests, Tukey HSD, was carried out to find which of the plant means was different from the other depending on a location. SPSS (version 15) statistical program was used for all statistical computations. Statistical significance was considered when P was equal to or higher than 0.05.

RESULTS AND DISCUSSION

There are three methods to check the validation of the results obtained. These are (1) the use of Standard Reference Material (SRM), (2) comparison of the results with those obtained by an independent method for the same

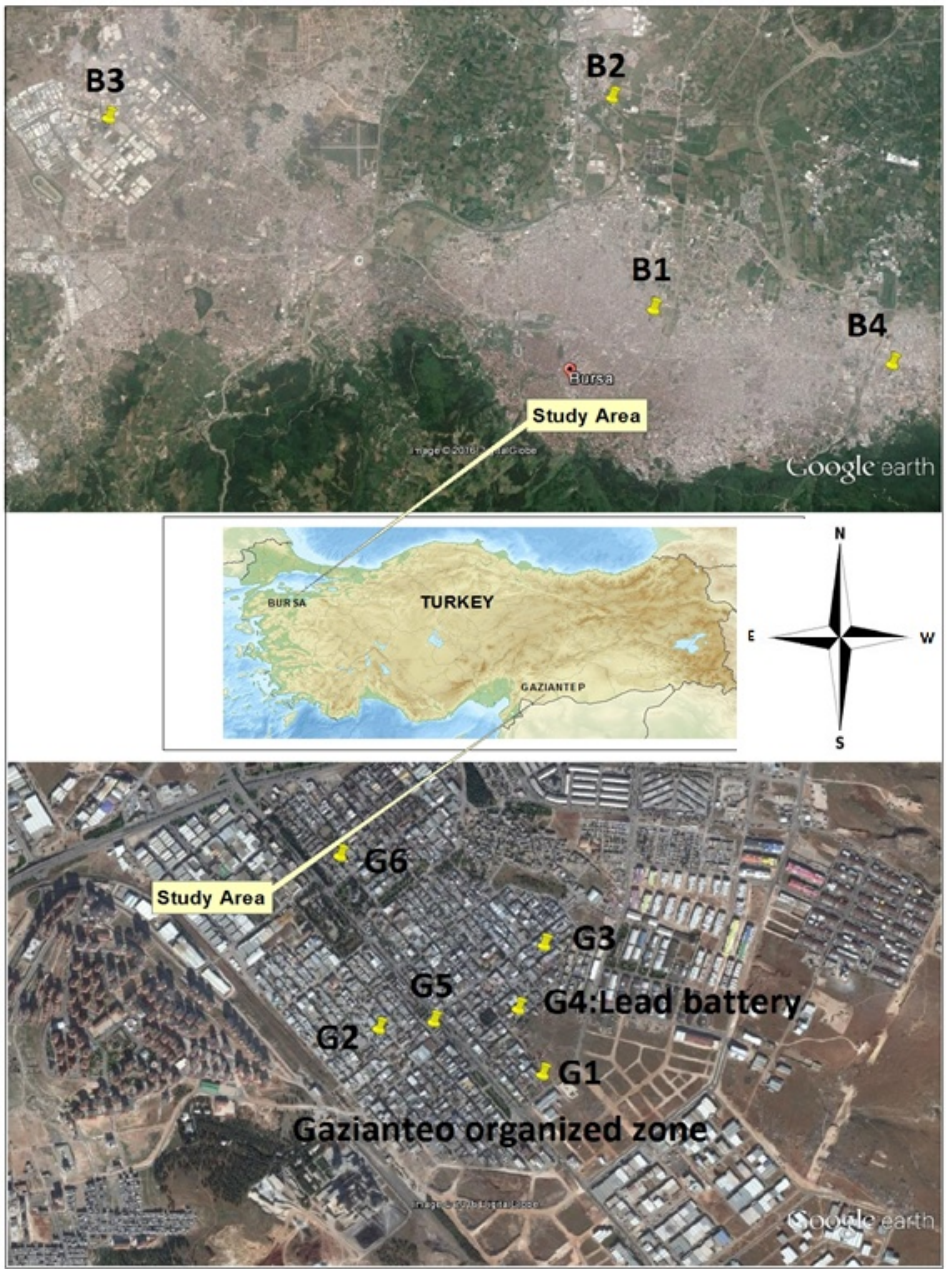

Fig. 1. Map of sampling locations: B1 – Bursa's industrial zone, in the city center; B2 – Bursa, the Demirtas industrial zone; B3 – Bursa, the Nilufer industrial zone; B4 – Bursa, Gursu's industrial zone; G4 – Around stopped lead battery center-distance 50 m; G1 – Gaziantep city, 200 m South direction away from G4; G2 – Gaziantep city, 400 m West direction away from G4; G3 – Gaziantep city, 200 m North direction away from G4; G5 – Gaziantep city, 200 m West direction away from G4; G6 – Gaziantep city, 1000 m Northwest direction away from G4

samples, and (3) the recovery test. In this study, the first method was used for the accuracy check of the quantitative determination of Cr and V, and the third method was used for the histidine determination by HPLC-MS. Concentrations of metals in SRM, "Bush branches and leaves-Trace elements (NCS DC73348)", were found to be 2.1 mg Cr kg^{-1}, 2.2 mg V kg^{-1}, 3010 mg S kg^{-1} while the certified value is 2.3 mg Cr kg^{-1}, 2.4 mg V kg^{-1} and 3200 mg S kg^{-1} (Table 1). Because the recoveries of more than 90% were achieved, Cr, V and S determinations in this study were considered as accurate. Effects of contamination were eliminated by subtracting the values obtained from the blank.

The concentrations of chromium and vanadium were given in Table 1. Taking into consideration chromium levels in *Salix matsudana* compared to *Platanus* L., *Cupressus arizonica* and *Eleagnus angus* collected from the same site (B2), it can be clearly concluded that *Salix matsudana* leaves have hyperaccumulator potential for chromium. The high concentrations of chromium of more than 10 000 μg kg^{-1} in *Salix matsudana* leaves taken from Bursa, Turkey, may be attributed to the intensity of industrial activities (there are more than 50 metal factories) in this city. Kendall et al (2011) reported that – unlike vanadium – chromium concentrations in airborne particulate matter taken from Bursa were higher than in urban areas of the USA and Spain. Guleryuz et al. (2008) determined chromium levels between 10 and 15 mg kg^{-1} for leaves of *Polygonum lapathifolium* taken from Bursa. Further, *Pinus nigra* L. and *Thuja* species as well as *Grass* may be considered as hyperaccumulators for vanadium.

Under normal conditions, concentrations of chromium and vanadium in plants are less than 1.0 and 0.5 mg kg^{-1}, respectively (Kabata-Pendias 2011). Avci et al. (2013) reported chromium concentrations (mg kg^{-1}) in ranges of 0.9-2.1 for *Platanus* L., 0.1-6.6 for *Pinus nigra* L., 1.1-2.9 for *Thuja (Cupressaceae),* 0.7-1.7 for *Cupressus*, 0.2-1.9 for *Vitis vin.,* 0.7-3.3 for *Nerium olean.,* 0.9-4.3 for *Acacia robinia,* 0.3-2.5 for *Populous nigra,* and 0.4-1.4 for *Cedrus libani* leaves grown around a lead battery factory. They obtained these results in 2006-2007. Four years later, the values achieved in this study for the same area are given in Table 1. The changes in Cr concentrations of plant leaves depending on years (from 2007 to 2011) were given in Figure 2. From this Figure, it is seen that the observed Cr levels in 2011 for *Thuja* and *Nerium oleander* are higher more than two-fold compared to 2007, while opposite results are obtained for *Pinus nigra* and *Acacia* leaves. Qian et al. (2014) determined vanadium concentrations in six dominant plant species (three perennial herbaceous species and three deciduous woody species) collected from 22 stations in the Liberty State Park located in the densely populated city of Jersey City close to the borough of Manhattan, New York. They reported that their study area had been used for railroad transportation and coal storage for over a century. Thus, they found much higher vanadium concentrations in the range of 2.06-11.6 mg kg^{-1}, compared to our results. Khan (2001) reported chromium concentrations up to 188 mg kg^{-1}

Table 1

Concentrations of histidine (His.), Cr, V and S in the samples analyzed

Plant species	**Sampling site**	**His.**[#] mg kg^{-1}	**Cr,** [*] µg kg^{-1}	**V,**[**] µg kg^{-1}	S,[***] mg kg^{-1}	**r,** his-Cr	**r,** Cr-S	**r,** his-V	**r,** V-S
1	2	3	4	5	6	7	8	9	10
Juglans regia L.	G1	7±1	2187	300	1147	0.52	0.63	0.51	0.79
	G2	8±1	2110	367	1052				
	G3	9±1	2061	300	967				
	B2	9±1	2367	382	1786				
	B4	8±1	2545	400	2185				
	control	7±1	784	245	945				
Platanus L.	G6	5±1	2089	162	2329	-0.16	-0.002	-0.06	0.12
	B1	2.0±0.3	3622	200	1938				
	B2	3±0.5	1093	179	2063				
	B4	4±1	892	120	3046				
	control	2.0±0.2	761	103	1078				
Pinus nigra L.	G1	4±1	2314	322	1032	0.49	0.41	0.27	-0.17
	G3	4±1	2105	351	874				
	G4	7±1	2848	500	1032				
	G6	4±1	2239	400	984				
	B1	1.0±0.2	1750	200	1000				
	B2	2±0.2	3059	800	844				
	B3	6±1	1938	440	813				
	control	1.0±0.1	347	195	805				
Thuja (Cupressaceae)	G1	8±2	5618	695	751	0.99	0.66	0.91	0.87
	G3	10±2	6803	1100	839				
	G4	7±2	3582	938	816				
	G6	5±1	2357	500	787				
	control	3±1	526	375	705				

cont. Table 1

1	2	3	4	5	6	7	8	9	10
Salix matsudana	B2	13±2	10484	640	6484	0.77	0.72	0.38	0.31
	B4	15±3	5679	300	8762				
	control	6±1	638	267	984				
Cupressus arizonica	G3	7±1	2215	415	819	-0.15	0.72	-0.98	0.83
	G5	5±1	2071	384	852				
	G6	6±1	1895	348	815				
	B1	3±1	2370	500	892				
	B2	10±2	1606	230	758				
	B4	3±0.3	1872	600	1375				
	control	1±0.3	269	206	769				
Eleagnus angustifolia L.	G1	23±2	3600	300	2754	0.95	0.58	0.78	0.3
	G2	15±3	1700	60	2525				
	G3	14±2	1976	115	2287				
	B1	12±2	1600	100	3206				
	B2	11±2	1700	80	2478				
	B3	8±1	1600	100	2938				
	control	3.0±0.3	293	65	1169				
Vitis vinifera L.	G1	10±2	1882	178	1155	0.60	0.22	-0.16	0.008
	G4	33±6	2000	200	1279				
	G5	11±2	1820	650	1901				
	B2	27±6	1693	217	2962				
	B3	25±5	1400	120	3275				
	control	2.0±0.2	237	110	927				
Nerium oleander L.	G3	11±2	3894	451	1089	0.69	0.90	0.86	0.71
	G4	9±1	7000	500	1770				
	G6	6±1	2300	230	1148				
	B2	8±1	1935	328	1209				
	control	3.0±0.3	582	221	951				

cont. Table 1

1	2	3	4	5	6	7	8	9	10
Robinia pseudoacacio L.	G3	10±1	1980	640	2327	0.65	0.86	0.34	0.32
	G5	7±1	2046	523	1917				
	G6	11±2	1708	630	1765				
	B3	11±2	1800	200	2355				
	B4	13±2	2200	500	2769				
	control	6±1	746	184	1179				
Populous nigra L.	G1	10±2	2600	40	3344	0.85	0.57	0.38	0.53
	G5	10±2	1700	100	1410				
	B1	7±1	1900	100	2750				
	B2	10±1	1984	200	1469				
	B3	10±1	1650	583	3746				
	control	2.0±0.3	279	50	1079				
Grass	B3	5±0.6	2900	1000	2523				
Cedrus libani	B3	4±1	2300	500	1121				
	control	2±0.3	198	265	1080				
SRM: Bush branches and leaves-NCSDC73348	certified (μg kg^{-1})		2300	2400	3200				
	found		2100	2200	3010				

*standard deviations for Cr are in the range of 12-20%, ** standard deviations for V are in the range of 8-20%, *** standard deviations for S are in the range of 10-22%;

The values for histidine were taken from elsewhere (Akkus, Yaman 2016*a*,*b*,*c*,*d*).

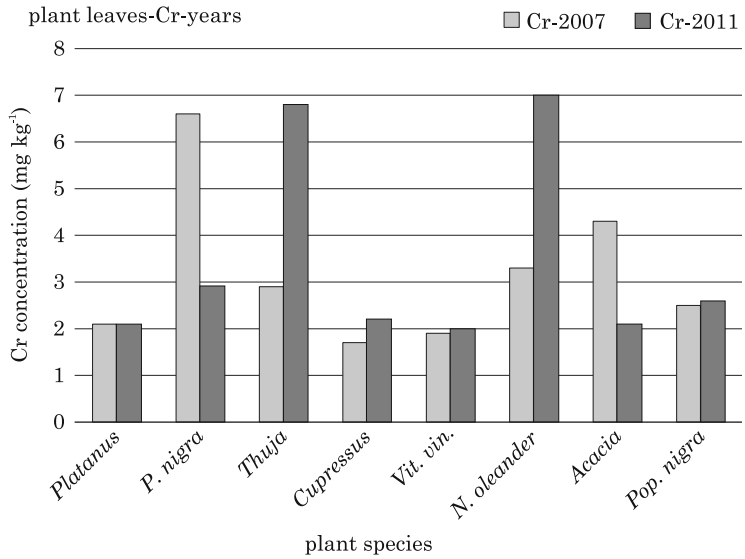

Fig. 2. Changes in Cr concentrations of plant leaves depending on years

in leaves of *Acacia Arabica* plant growing on the tannery effluent-contaminated soil. Liu et al. (2005) determined eight metal concentrations in 21 plant species growing on hills near the Beijing Steel Factory (BSF) and 17 plant species in the Beijing Botanical Garden (BBG). They found chromium concentrations in ranges of 0.55-1.03 mg kg^{-1} for those plant samples. Sinam et al. (2011) compared the accumulation of Cr(VI) and biochemical changes in tolerance to metal induced stress in *Cucumis utillissimus* L. grown in chromium contaminated soil (CS) with garden soil (GS). They reported that accumulation of Cr in the leaves of the plant increased with increase in substrate metals concentration.

Hyperaccumulation has been recognized as an extreme physiological response in heavy metal tolerance. In other words, hyperaccumulator plants can tolerate much higher metal concentrations without symptoms of toxicity (Bargagli 1998, Mulgrew, Willeams 2000, Mertens et al. 2005, Verbruggen et al. 2009). However, the physiological processes involved in hyperaccumulation have not been well understood. Plants must be able to store the metal ions in nonlabile complexes so as to eliminate toxic effects. The most likely areas for storage are the cell wall, the cytosol and the vacuole. A number of steps are required for metal ions to reach the storage tissues: mobilization and uptake from soil, compartmentation and sequestration within roots, transfer to the xylem for transport, distribution between metal sinks in aerial plant organ tissues and sequestration as well as storage in leaf cells (Clemens et al. 2002). Each stage could affect metal accumulation. It was

reported that the sulfate transporter played an active role in the chromium uptake in cells of higher plants (Singh et al. 2013). The hyperaccumulator may be detoxifying the metal in the leaves via strong binding ligands. Therefore, ligands, including histidine, cysteine and phytate, may play a part in sequestration within isolated compartments (Krämer et al. 1996, Hall 2002, Callahan et al. 2006, Haydon, Cobbett 2007). The high metal uptake may be attributed to highly efficient intracellular compartmentalization. Due to high toxic and even carcinogenic effects of metals, including cadmium, lead, nickel, chromium and copper, for humans and animals, numerous studies have been carried out in order to determine their concentrations in environmental and biological matrices (Ozen et al. 2003, Yaman, Bakirdere 2003, Yaman, Cokol 2004, Yaman et al. 2007, Er et al. 2013, Yaman 2014, Ugulu 2015, Akkus, Yaman 2016*a*,*b*,*c*,*d*).

CONCLUSIONS

The results of this study cast the light on the extent of anthropogenically altered environments of highly industrialized cities. Furthermore, the results give a hint about the bioaccumulation of chromium and vanadium by *Juglans regia* L., *Platanus* L., *Pinus nigra* L, *Thuja (Cupressaceae), Salix matsudana, Cupressus arizonica, Eleagnus ang., Vitis vin., Nerium olean., Robinia pse. Populous nigra, Grasses and Cedrus libani* leaves. Chromium concentrations up to 10 484, 7000 and 6803 μg kg^{-1} were found, respectively, in leaves of *Salix, Nerium olean.,* and *Thuja (Cupressaceae)* taken from organized industrial zone in Bursa and Gaziantep cities. Taking into consideration the tolerance to chromium (2.0 mg kg^{-1}) in plant leaves, these concentrations are considerably higher. The lowest chromium concentrations in control samples of *Salix, Nerium olean.,* and *Thuja (Cupressaceae)* were found to be 638, 582 and 526 μg kg^{-1}, respectively. Hence, the ratios of the highest to the lowest chromium concentrations (Table 1) for these plant species are 16.4, 12.0 and 12.9-fold, and it seems that these plant leaves have a potential as a biomonitor and/or hyperaccumulator. Similarly, the ratios of the highest to the lowest vanadium concentrations (Table 1) for plant species are 2.9 for *Thuja*, 4.1 for *Pinus nigra*, 5.9 for *Vitis vin.* and 3.5 for *Robinia pseu.*-fold. Thus, these plant leaves may be considered as biomonitors and/or havong the hyperaccumulator potential for vanadium.

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