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Bioaccumulation of Heavy Metals in Urban Tree Leaves

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LEAVES of nine tree species (*Pinus halepensis* Mill, *Pinus sylvestris* L., *Cupressus italica*, *Cupressus arizoneka* Greene, *Quercus robur L.*, *Quercus ilex* L., *Ficus nitida* L., *Eucalyptus globulus Labill* and *Casuarina equisetifolia* L.) were used to inspect accumulation of heavy metals emitted at areas with different pollution load in Baku (Azerbaijan). Concentrations of Cr, Cu, Mn, Pb, Zr, Ti, V, Bi, Cd, Ni, and Zn were determined by inductive coupled plasma (ICP-MS) and EDRF (energy dispersive X-ray fluorescence). Concerning Fe, Cd, Cu, Pb, Zn and Zr concentrations, the ICP results declared a relative increase. Unlike the rest species, the concentration of Ni in *E. globulus*, *C. equisetifolia, F. nitida* and *C. italica* leaf samples was higher than 10mg/kg, which is the beginning of toxic concentration. V concentration still in the normal range (0.2–1.5mg/kg). All tested tree leaves have Cr concentration within the toxic range (<5mg/kg), except *P. halepensis*, *P. sylvestris* and *C. italica* trees. The results showed a relatively high content of Zr in genus Quercus, ranging from 0.15 to 3.13ppm. The results of EDRF were slightly different, where higher Cu (8.07%), Zn (38.6%), I (55.12%) and Co (4.86%) characterizes the industrial site, whereas areas of high traffic dominated by elevated concentrations of Pb (9.91%), Cd (0.29%), Mo (0.17%) and Cr (59.05%). These variations enhanced the idea that these sites were influenced by different sources of pollution. The findings may be useful for future surveillance as preliminary reference values for levels of heavy metals in urban and industrial settings.

Keywords: Air monitoring, Bio-indicators, Heavy metals, Needles, Tree leaves.

Introduction

Rapid and unorganized urban and industrial developments have created substantial environmental pressures on urban areas in developing countries (Kumar, 2013). Air and soil compositions, dominated by emissions from industrial plants and automobile exhaust, have significantly elevated levels of heavy metals in urban areas (Kleckerová & Dočekalová, 2014). Among the pollutants in the atmosphere, heavy metals such as Pb, Cd, Cr, Mn, Ni, Cu, Zn and As are an significant problem owing to their toxic impacts and accumulation throughout the food chain, leading to severe problems in the environment and health (Cocozza et al., 2016; Sasi et al., 2019). The primary sources of Cd, Ni, Cu and Zn pollution are oil, pneumatics and old car remains, whereas Mn has a predominant natural source (Malizia et al., 2012). Co, Ni, and V are released from sources such as petrochemical and gas industries into the environment and Pb comes from commercial activities and small industries (Delshab et al., 2017; Naeimi et al., 2018). They can be transported over long distances that cause local, regional or global pollution, even in pristine areas like the Polar Regions (Mohy El-Din, 2017). By moist and dry deposition, these components return to the earth's surface and can harm soil, water, and plant productivity depending on their concentrations (Chen et al., 2013; Stankovic et al., 2014).

Plants are essential components of ecosystems and may improve the quality of urban environments (Akbari, 2002; Brack, 2002). Plants can take up and accumulate heavy metals through their root and leaf surfaces (Sawidis et al., 2001). Positive interactions have been recognized between atmospheric heavy metal deposition and plant heavy

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metal levels (Ugulu et al., 2012) and many plant species are capable of absorbing and accumulating important amounts of possibly toxic substances (Piczak et al., 2003).The features of using plants are that (a) They are cost-effective solutions to filtration air sampling, (b) They provide helpful information for designing deposition surveillance networks, (c) They provide an integrated exposure measured over a certain period of time and (d) They significantly promote the analytical determination of trace elements (Bosco et al., 2005; Youssef et al., 2013). Bark and leaf were commonly used for biomonitoring metals compared to other components of the tree/shrub, such as buds, flowers and needles as their structures can absorb more air pollutants (Matin et al., 2016; Oliva & Mingorance, 2006). The capacity of foliage accumulation by dry or wet deposition or absorption depends strictly on the spatial distribution of the trees, the duration of exposure and climate, but also on the characteristics of the species, such as the leaf area (single leaf and whole leaf), the surface texture (roughness and pubescence), the habitus of the plants (evergreen or deciduous) and the exchange of gas (rate between leaf and atmosphere, multiple stress responses) (Alfani et al., 1996; Beckett et al., 2000; Liu et al., 2012; Cocozza et al., 2013). Most of the above research, however, regarded only one single tree species (Aksoy et al., 2000; Mingorance & Oliva, 2006; Al-Alawi & Mandiwana, 2007) and few surveys concurrently studied various plant species (Piczak et al., 2003), particularly evergreen and perennial species (Hu et al., 2014).

Several examples of trees/needles used as biomonitors for urban environment air and soil pollution, e.g. (Ukpebor et al., 2010), *Phoenix dactylifera* (Aksoy & Özturk, 1996), *Pinus sylvestris* (Dmuchoswski & Bytnerowicz, 1995), *Pinus pinea* (Lombardo et al., 2001; Dongarra et al., 2003 a), *Pinus massoniana* L. (Kuang et al., 2007), *Nerium oleander* (Dongarra et al., 2003 b), *Pittosporum tobira* (Lorenzini et al., 2006), *Acacia retinides* and *Eucalyptus torquatain* (Pyatt, 2001), *Populus nigra* (Djingova et al., 2001), *Tibouchina pulchra* (Moraes et al., 2003), in addition to several other tree species (Lau & Luk, 2001; Baycu et al., 2006). Furthermore, several species of plants were already used as bioindicators (Aksoy et al., 2000; Celik et al., 2005; Mingorance & Oliva, 2006). *Acer pseudoplatanus* L., for instance. Bioindicator used to evaluate air contamination in urban ecosystems in Europe (André et al., 2006) *and Quercus ilex* L. Was used as a heavy metal bioaccumulator in urban regions (Ugolini et al., 2013). It is necessary to evaluate the potential for greening plant species to remove heavy metal contaminants from environmental matrices with large centralized anthropogenic activities (Hu et al., 2014). The aims of this research were: (1) To evaluate The levels of certain poisonous metals (Cr, Cu, Mn, Pb, Zr, Ti, V, Bi, Cd, Ni and Zn) in the leaves of prevalent green species in Baku; (2) To evaluate the total metal accumulation capacities of plants and (3) The findings may be useful for future surveillance as preliminary reference values for levels of heavy metals in urban and industrial settings.

Materials and Methods

Study area

Baku is the capital and largest city of Azerbaijan, as well as the largest city on the Caspian Sea and of the Caucasus region. Baku is located on the Caspian Sea's west shore. There are several mud volcanoes in the area of the city (Keyraki, Bogkh-bogkha, Lokbatan and others) and salt lakes (Boyukshor, Khodasan and so on). Baku has a semi-arid subtropical climate with warm and dry summers, cold and sometimes humid winters, and strong winds throughout the year. Baku does not see highly warm summers, however, unlike many other towns with this environment. This is mainly due to its northern latitude and its location on a peninsula on the Caspian Sea coast. The most aridest part of Azerbaijan is Baku and the Absheron Peninsula (precipitation here is about 200mm (8 in) per year). Baku's largest industry is oil and its exports of petroleum make it a major contributor to the balance of payments of Azerbaijan. As a Soviet industrial center, the past of the city has left it one of the world's most polluted cities (Agayev, 2007). The average daily mean temperature in July and August is 26.4°C (79.5 °F), according to Window to Baku (2010).

The sampling sites categorized into three main areas: (I) High polluted area (HPA) including two urban zones with high traffic density, (II) Low polluted area (LPA) including two petro chemicalindu strial close to Absheron peninsula), and (III) Control area (Cont.) including two rural zones (botanical garden of Baku).

Reagents

All acids and reagents used in this study, such as perchloric acid (90%) and nitric acid

(65%), were of super-pure quality (Merck Co., Germany). All glassware was washed with acid by soaking in dilute nitric acid and rinsed before use with deionized water.

Leaves collections

The most common trees in the studied areas such as *Pinushalepensis*, *Pinussylvestris*, *Cupressusitalica*, *Cupressus arizoneka*, *Quercus robur*, *Quercus ilex, Ficus nitida; Eucalyptus globulus* and *Casuarinas equisetifolia*, were selected.

To avoid micro-scale differences in locations, a sampling area of 100m max.100m was regarded at each site. Trees with the same era were used for sampling to have the same integration time of metal pollution. Every tree species with similar height, trunk diameter, and the cone was selected for this purpose. At the time of sampling, all selected trees were about 5 years old (Sawidis et al., 2011). For leaf sampling, leaves of the same length were regarded as samples, fully expanded and without spots or unusual appearance (chlorosis or necrosis). Trees with unique leaves and barks (e.g. wrinkled or yellow leaves and pestle barks) Excluded were. Also, it was not regarded as the trees that had honeydew. Care was taken to prevent leaf selection with imperfections such as falling birds, an infestation of insects, and treatment of pesticides. Leaves were randomly gathered from each tree/ shrub's reduced two-thirds canopy. The samples were placed in polyethylene bags until drying at 4° C (Sawidis et al., 2011).

Preparing of leaf samples for ICP analysis

Leaves are dried in the furnace, pulverized in a mortar and passed through a 300mm sieve. Approximately 250mg of the powder was used for digestion in glass ships with 6ml of nitric acid (65 percent, Sigma Aldrich) and 2ml of H_2O_2 (30 percent, Sigma Aldrich) using EPA technique 3051 (EPA, 2007; Enamorado-Baez et al., 2013). Closed vessels were placed in themicrowave system (Discover SP-D, CEM corporation, US), equippedwith 24-places and auto-sampler, andindividually processed. The volume of each sample is adjusted to 25ml after cooling and ultrapure deionized water is added. Each sample has been digested three times and readings are recorded on average. In addition to each sample, a control sample was also used to determine background pollution during digestion. The standard solution of each heavy metal studied was used to verify the precision of the methodology and to guarantee the removal of heavy metals from the tree, and the retrieval rates of the metals were achieved. The concentrations of chromium (Cr), copper (Cu), manganese (Mn), lead (Pb), zirconium (Zr), titanium (Ti), vanadium (V), bismuth (Bi), cadmium (Cd), nickel (Ni) and zinc (Zn) in leaf samples were eventually measured using Inductively Coupled Plasma (ICP-MS) and (ICP OES)**.**

Metal analysis by EDRF

For Metal analysis by EDRF technique, after drying and pulverizing, represented a sample of each sampling area (HPA, LPA and control area) used for trace metals analysis by Energy dispersive X-ray fluorescence (EDRF). Qualitative and quantitative elemental analyses of the samples were performed by using X-ray microscope XGT-7000. XGT-7000 - Energy dispersive X-ray fluorescence (EDRF), a microscope with a system of partial/complete evacuation of the sample allows for elemental analysis of sodium (Na) to uranium (U) selected in the image of the particles, two-dimensional mapping of the signals in the spectrum of X-ray fluorescence allows imaging of particles in visible light and transmitted x-rays, has a system of partial vacuum (for the precise determination of light elements in the samples, poorly tolerate a vacuum), as well as the complete evacuation of the sample (for the most accurate determination of light elements), an analysis of the macro (10cm x 10cm) and micro (10mkm x 10mkm) dimensional objects, is the software (with the editing capabilities of two-dimensional images and a set of tools for quantitative elemental analysis), a database of SLICE for the rapid identification of materials.

Statistical analysis

Data were elaborated by using the software Statistics. Principle Component Analysis (PCA) may provide useful information on the relationship between leaves, species, sampling areas, the concentration of elements and their potential sources.

Results and Discussions

Metals analysis using ICP

The concentrations of Cr, Cu, Mn, Pb, Zr, Ti, V, Bi, Cd, Ni and Zn (mg/kg dry weight) of the plant samples of each area are shown in Table 1. As depicted in this Table, the highest (3.60mg/kg) at HPA and the lowest (0.041mg/kg) at LPA concentrations of titanium in the leaf samples were found in *Q. robur* and *F. nitida*, respectively. Ti is still far from being accepted as an essential element to plants (Wild & Jones, 1988). Levels of Ti in plants vary rather considerably within the range of 0.15 to 80ppm. Consequently, the concentration of titanium in this study still in the normal range (Kabata-Pendias & Pendias, 2010). The highest concentration of vanadium was found in HPA in *C. italica* (0.999mg/kg) and the lowest vanadium concentration was also seen in LPA in *F. nitida* (0.001mg/kg). Some species recorded zero vanadium concentration like *P. halepensi* and *E. globulus*. The permissible concentration range of vanadium in plants and trees is 0.2–1.5mg/kg and its toxic concentration is 5–10mg/kg (Kabata-Pendias & Pendias, 2010). Consequently, the concentration of vanadium in this study still in the normal range. In Table 1, the maximum concentration of iron was seen in the *F. nitida* leaf located at HPA (19.284mg/kg). In contrast, the lowest concentrations of iron were determined in LPA in the leaf of *P. sylvestris* (0.903mg/kg). The highest concentrations of copper were found in HPA in the *Q. ilex* leaf (20mg/kg) and in the leaf sample of the *E. globulus* species in the same area (19.7mg/kg). While the minimum copper concentrations were seen in the *C. italica* leaf (5.4mg/kg) and in the *Q. robur* leaf (7.6mg/kg) in LPA. According to the previous studies (Kabata-Pendias & Pendias, 1992; Borkert et al., 1998), the concentration of Cu in plant tissues ranged from 5 to 20µg g^{-1} d. w. If the concentration exceeds the upper limit (20µg g^{-1} d. w), toxicity effects are likely to occur. Regarding cadmium results, the highest (17.7 and 14.02mg/kg) concentrations were measured in *Q. robur* and *E. globulus*r, espectively in HPA. The lowest (1.8mg/kg) concentration was determined in *C. arizoneka* in LPA. Cd level that recorded in the present study showed that Cd level exceeds the upper limit of the US Environmental Protection Agency (EPA, 2006) of 0.002mg/kg within toxic range for plants. Papa et al. (2012) reported that the Cu, Pb and Cd contents of *Q. ilex* leaves were markedly higher at the urban sites than at the control site.

As presented in Table 1, the highest concentrations of lead were observed in the leaf sample of *E. globulus (*77.2mg/kg) in HPA and *F. nitida* (65.7mg/kg) in the same area. The lowest concentration of lead was measured in the leaf of *C. italica* (2.2mg/kg) and in *Q. robur* (2.3mg/kg) in LPA. These results reflect the fact that leaves of *E. globulus* and *F. nitida* have a very high capability for the accumulation of Pb than the other plant species. The level of lead of the tree species leaf from the locations studied surpassed 50mg/kg. The lead level of 35–52mg/kg in pine leaf specimens was also recognized by Matin et al. (2016) during surveillance of cadmium, lead and arsenic in industrial areas in Azerbaijan. The permissible or normal concentration of lead in trees is between 0.1 and 5mg/kg and 10–100mg/kg is toxic (Kabata-Pendias & Pendias, 2010). Our data showed that lead concentrations of the following species have surpassed the standard limit and are toxic in *E. globulus*; *F. nitida* and *Casuarinas equisetifolia* in HPA. It has been recorded that less than 2% of lead in leaves and branches comes from roots and approximately 98% comes from the atmosphere (Hovmand et al., 2009). Other studies have shown that transferring lead from root to leaf is not a significant contamination trend and trees can readily absorb atmospheric lead by deposition Pb-laden particulate matter on their leaves (Ribeiro de Souza et al., 2012; Turer et al., 2001).

The present findings indicate that Baku has very elevated accumulation values of copper, iron, and lead. This can be ascribed to the reality that the town is more populated, contributing to heavy metal pollution by cars and industrial activities.Industrial and metallurgical procedures as well as diesel fuel combustion generate the biggest emissions of lead that have no known physiological function in plants and can be harmful. It is known that the main sources of copper, iron, and lead pollution are the steel industry and coal combustion (Bargagli, 1998; Anicic et al., 2011). As depicted in Table 1, the highest nickel concentrations (17.5 and15.8mg/kg) in the leaf samples were found in *E. globulus* and *Casuarinas equisetifolia,* respectively in HPA, while the lowest concentration (0.78mg/kg) was recorded in LPA in *Q. robur* leaf. The normal concentration of nickel in trees is 0.1–5mg/kg and is 10–100 mg/kg toxic (Kabata-Pendias, 2010). The concentration of nickel in *E. globulus*, *Casuarinaequisetifolia*, *F. nitida* as well as *C. italic* leaf samples were greater than the toxic concentration of 10 mg/kg. The concentration of nickel of the remaining species was greater than 5 mg / kg but did not achieve the 10 mg/kg limit, which is the start of toxic concentration. These species absorbed nickel more than the ordinary amount of nickel.

TABLE 1. Mean value ((mg/kg) of heavy metal contents of plant species leaves collected from HPA, LPA and control area.

Plant species	Location	Ti	V	Fe	Cu	Pb	Bi	Zn	Zr	Cd	Cr	Ni	Mn
	P.h. Cont.	0.063	-	0.272	3	0.72	0.003	0.0229	0.03604	1.4	2.6	0.52	0.399
Pinus halepensis	P. h. LPA	0.181	0.43	0.903	10	2.5	0.0497	0.1801	0.382	5.4	10	1.8	0.992
	P. h. HPA	0.772	0.55	1.924	12	6.72	0.071	0.2281	0.8 1	8.9	12.98	3.50	0.104
	P. s. Cont.	0.0132	0.002	0.227	8.01	1.2	0.0016	0.05017	0.0237	0.27	0.65	0.81	0.0267
Pinus sylvestris	P. s. LPA	0.183	0.13	2.158	12	2.5	0.0117	0.1577	0.311	3.4	5.9	1.3	0.257
	P. s. HPA	0.٣98	0.611	3.122	14	3.3	0.0199	0.2397	0.713	5.1	7.5	2.7	0.351
	C. i. Cont.	0.026	0.0024	0.176	5.9	0.5	0.0026	0.01541	0.0023	0.18	0.10	1.2	0.0155
Cupressus italica	C. i. LPA	0.279	0.216	0.965	5.4	2.2	0.017	0.1869	0.121	2.18	1.8	4.6	0.094
	C. i. HPA	0.٩56	0. 996	1.844	12.3	3.48	0.033	0.1966	0.583	3.20	5.70	9.62	0.194
	C. a. Cont.	0.0032	0.0098	2.268	3.5	1.1	0.0018	0.02825	0.0128	0.11	1.2	0.49	0.214
Cupressus arizoneka	C. a. LPA	0.216	0.13	6.379	9.5	4.1	0.049	0.2617	0.32	1.88	3.0	1.7	0.291
	C. a. HPA	0.٨59	0.457	10.191	17	5.8	0.109	0.3047	0.79	7.2	4.3	2.0	0.689
	Q. r. Cont.	0.031	-	0.713	6.3	1.5	0.01307	0.1834	0.0032	0.84	0.18	0.12	0.0149
Quercus robur	Q. r. LPA	1.3	0.17	3.027	7.6	2.3	0.188	0.696	0.15	5.9	1.7	0.78	0.139
	Q. r. HPA	٣.60	0. 8	3.887	11	6.8	0.922	0.8513	0.76	14.02	2.2	1.3	0.638
	Q. i. Cont.	0.001	0.011	1.614	9.6	1.1	0.0997	0.2683	0.85	0.28	0.28	1.2	0.233
Quercus ilex	Q. i. LPA	0.30	0.15	5.581	12.6	4.9	0.1052	0.7312	1.21	3.23	2.9	2.8	0.381
	Q. i. HPA	0.٨٨	0.4	10.228	20	6.4	0.1223	0.9957	3.13	6.23	4.6	3.2	0.475
	C. e. Cont.	0.088	0.0046	8.014	6.7	19.82	0.0988	1.1239	0.08	0.14	0.92	2.51	3.09
Casuarinas equisetifolia	C. e. LPA	0.67	0.01	11.669	13	22.1	0.168	3.1589	0.13	8.8	2.5	9.8	8.167
	C. e. HPA	0.76	0.022	14.192	19	50.6	0.861	6.1779	0.36	9.9	2.7	15.8	14.187
	F. n. Cont.	0.0057	-	11.251	6.6	13.9	0.003	2.0917	0.014	1.8	1.2	3.00	2.062
Ficus nitida	F. n. LPA	0.041	0.001	15.078	9.7	28.9	0.012	9.2317	0.29	4.7	3.3	7.5	9.396
	F. n. HPA	0.070	0.08	19.284	15.5	65.7	0.028	12.2106	0.55	8.5	3.9	11.0	11.406
	E. g. Cont.	0.006	-	5.536	7.5	12.13	0.0024	2.1079	0.09	1.6	0.72	6.2	4.043
Eucalyptus globulus	E. g. LPA	0.057	0.015	11.847	9.19	46.1	0.015	5.1774	0.26	6.8	4.1	12.3	7.201
	E.g. HPA	0.07	0.033	14.839	19.7	77.2	0.033	9.2172	0.49	17.7	3.0	17.5	10.217

The highest (9.2172 and 12.2106mg/kg) concentration of zinc in the leaf was found in *E. globulus* and *F. nitida,* respectively in HPA and the lowest (0.1801 and 0.1869mg/kg) in LPA in *P. halepensis and C. italica* leaf, respectively. Zn is an essential component in all organisms and plays a significant role in enzyme, auxin and certain protein biosynthesis. The elevated concentrations of Zn in crops can cause manufacturing loss and their low concentrations can lead to deformation of the leaves (Safari et al., 2018)**.**

The highest (12.98 and 10mg/kg) concentrations of chromium were measured in *P. halepensis* leaves of both HPA and LPA, respectively, compared to the control. While, the lowest (1.8 and 1.7mg/kg) concentrations of chromium were measured in *C. italica* and *Q. robur* leaves, respectively, from LPA. According to the present results, the mean Cr concentration values werewithin the normal range for plants (0.1-0.5mg/kg) (Kabata-Pendias & Pendias, 2001). In the polluted sites, the values of Cr within *P. halepensis*, *P. sylvestris* and *C. italica* were higher than the normal range but were lower concentrations (<5mg/kg) than the toxic range for plants (5-30mg/kg) (Kabata-Pendias & Pendias, 2001). In the rest species, Cr concentrations were within toxic range for plants.

As presented in Table 1, the highest concentrations of manganese were observed in the leaf sample of *Casuarinas equisetifolia* in HPA (14.187mg/kg) and in *F. nitida* in the same area (11.406mg/kg). The lowest concentration of manganese in LPA was measured in the leaf of *C. italica* (0.094mg/kg) and in *Q.robur* (0.139mg/kg). According to Kabata-Pendias (2010), the critical Mn deficiency level for most plants ranges from 15 to 25ppm (DW), whereas the toxic concentration of Mn to plants is more variable, depending on both plant and soil factors. Generally, most plants are affected by theMn content around 500ppm (DW). However, the accumulation above 1000ppm (DW) also has been reported for several more resistant species or genotypes. Accordingly, in the present study, the values of Mn still in the normal range in all plant species at all sites.

As presented in Table 1, the highest (3.13mg/kg) concentration of Zr was measured at HPA in *Q. ilex* leaf. Except for this species, the concentration for all other trees/shrubs ranged from (0.121-0.491mg/kg) at all polluted areas. Although most soils contain considerable quantities of Zr, its accessibility for plants is very restricted. Gribovskaya et al. (1968) mentioned that Zr content in roots and nodules is higher than this in tops, which apparently indicates the low mobility of Zr in plants. Smith & Carson (1978) studied the history of plant-based stable Zr and ^{95}Zr and showed that soil-based Zr concentration variables are small in plants, while rainwater-based variables are much greater for both soil-based and epiphyte. This interprets the comparatively elevated content of Zr, varying from 0.15 to 3.13ppm in Quercus genus. Relative elevation values of As, Br, Cd, Cu, Hg, Mo, Pb, Zn, and Zr were noted in Baku city. Zn and Pb, however, are the most frequently enhanced metals in many cities' atmosphere.

The concurrent work suggested that, the highest (0.922mg/kg) concentration of Bi was recorded in *Q. robur* leaf at HPA. Plant Bi content was not widely researched (Kabata-Pendias, 2010). Bi is regarded as a rare metal in the Earth's crust (about 0.2ppm) and is generally discovered in certain metal-associated veins (e.g., Ag, Co, Pb, Zn). Bi is probable to be concentrated in contaminated locations because of its elevated concentration in certain coals and wastewater sludges. The capacity of distinct plants to absorb trace metals differs significantly; however, the index of their accumulating capacity shows some general trends when compared to a large scale.Some metals like Cd, B, Br, Cs, and Rb are highly easy to take on, while Ba, Ti, Zr, Sc, Bi andGa, were absorbed to some extent, Fe and Se are accessible to plants only mildly.These findings indicate that variations between plant species with respect to individual element levels may rely on the leaves morphological and anatomical parameters (Table 1) (Kardel et al., 2010; Liu et al., 2013).

Metal analysis using EDRF

The concentrations of the most abundant pollutants: Cr, Cu, Zn, Mo, Cd, I and Pbof testleaf samplesof high polluted area (HPA), low polluted area (LPA) and control area were determined by EDRF (Tables 2-4, respectively). These results are slightly different from those obtained by ICP. Where,the mass percentage of Cd of samples collected from HPA (traffic zone) lower than that of LPA (industrial zone) compared to the control samples as follow: 0.29> 0.72> 0.22 (%), respectively. The mass percentage of Pb in samples collected from HPA recorded a higher value than this of LPA compared to the control samples as follow: 9.91> 0.23> 0.03 (%), respectively. Also, the elements peaksof leaf samples collected from HPA are sharp (Fig.1 a) followed by those of LPA as shown in Fig. 1 b, while the lowest peaks of the elements appeared for those samples collected from the control area (Fig. 1 c).

Both areas (HPA and LPA) are highly metal polluted in comparison to the controlarea. The slight difference in metal concentration of both areas is related to industrial activities represented by enriched Cr and Cu concentrations. Traffic area is characterized by higher Cd, Fe and Pb contents confirming the automobile emissions source. Industrial facilities (chemical, pharmaceutical, metallic, petroleum) are distributed randomly in central parts of the region in the industrial area (LPA). They represent the sources of various types of pollutants together with city traffic and coal power stations (Mitrovic et al., 2008).

The statistical PCA analysis (Fig. 2) leads to the conclusion that leaves of *E. globules*; *casuarinasequisetifolia* and *F.nitida* are good bioindicators for Cu, Cd, Cr, Fe and Pb. While needle leaves of *P.halepensis*, *P.sylvestris C.arizoneka* and *Q.robur*, are good choice for V, Ti, Zr and Bi accumulation.Wang et al. (2011), reported a greater translocation factor (heavy metal content ratio in leaves to roots) for *Metasequoiaglyptostroboides*, also verified similar outcomes. This may suggest that broad-leaved plants play a significant role in eliminating air pollution.

TABLE 2. The mass percent and oxide formula of Cr, Cu, Zn, Mo, Cd, I and Pb in represented sample determined by EDRF collected from high polluted area (HPA).

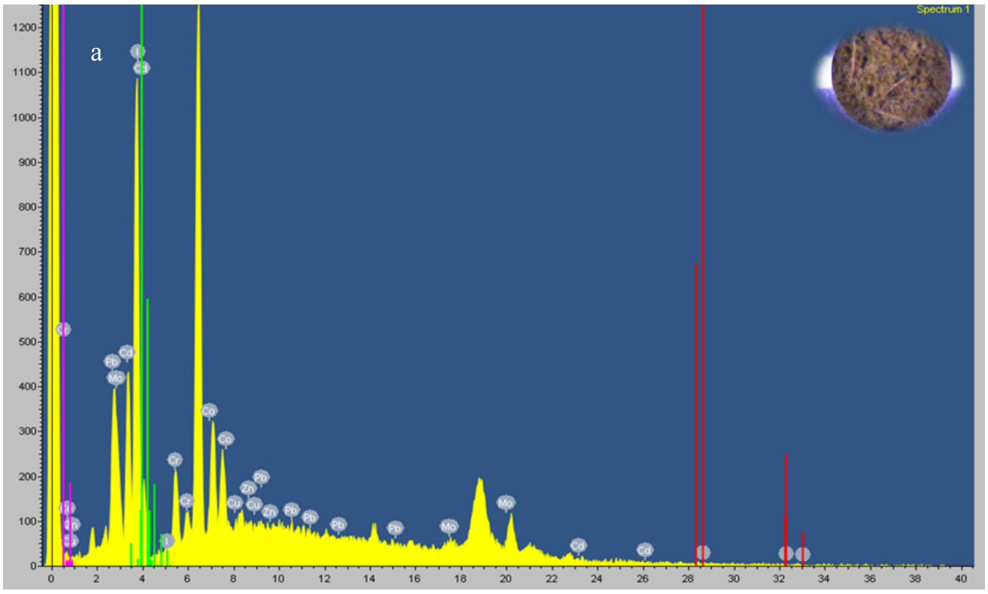
Element	Line	Mass (%)	Sigma	Atomic (%)	Intensity	Formula	Mass (%)	Molecule
24 Cr	K	59.05	52.42	37.88	13.65	Cr2O3	86.31	90.51
27 Co	K	0.00	12.97	0.00	0.00	CoO	0.00	0.00
29 Cu	K	0.00	10.05	0.00	0.00	CuO	0.00	0.00
30 Zn	K	0.00	14.36	0.00	0.00	ZnO	0.00	0.00
42 Mo	K	0.17	9.05	0.06	0.07	MoO3	0.25	0.2
48 Cd	k	0.29	26.24	0.08	0.02	CdO	0.33	0.4
53 I	k	1.85	45.68	0.49	0.06	I2O5	2.43	1.1
82 Pb	L	9.91	40.02	1.60	0.91	PbO	10.68	7.6
O		28.73	29.46	59.89				

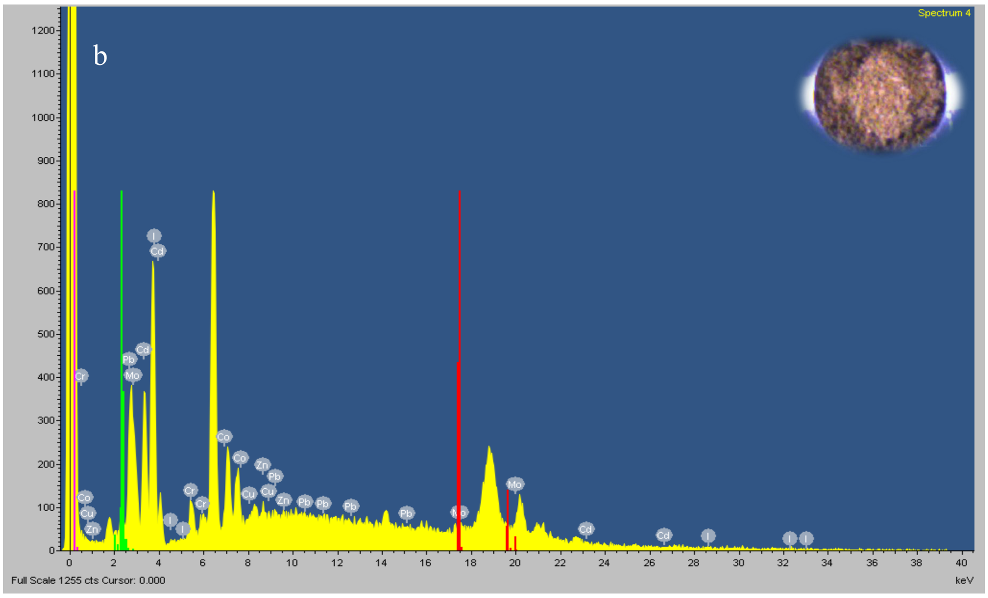
TABLE 3. The mass percent and oxide formula of Cr, Cu, Zn, Mo, Cd, I and Pb in represented sample determined by EDRF collected from low polluted area (HPA).

Element	Line	Mass (%)	Sigma	Atomic (%)	Intensity	Formula	Mass (%)	Molecule
24 Cr	K	0.25	33.91	1.38	0.03	Cr2O3	0.25	0.6
27 Co	K	1.85	26.53	6.72	0.38	CoO	2.35	4.0
29 Cu	K	1.04	26.49	25.15	0.23	CuO	1.31	2.1
30 Zn	K	37.46	106.48	0.07	8.47	ZnO	46.63	73.5
42 Mo	K	0.15	23.48	0.28	0.04	MoO3	0.23	0.2
48 Cd	k	0.72	65.19	12.67	0.05	CdO	0.82	0.8
53 I	k	36.63	108.53	0.05	0.58	I2O5	48.17	18.5
82 Pb	L	0.23	137.55	59.47	0.01	PbO	0.24	0.1
O		21.67	47.78					

TABLE 4. The mass percent and oxide formula of Cr, Cu, Zn, Mo, Cd, I and Pb in represented sample determined by EDRF collected from control area.

Element	Line	Mass (%)	Sigma	Atomic (%)	Intensity	Formula	Mass (%)	Molecule
24 Cr	K	55.27	26.37	34.31	27.81	Cr2O3	80.78	76.8
27 Co	K	0.00	8.02	0.00	0.00	CoO	0.00	0.00
29 Cu	K	0.01	8.97	0.01	0.01	CuO	0.02	0.0
30 Zn	K	8.68	8.89	4.29	4.59	ZnO	10.81	19.2
42 Mo	K	0.07	4.09	0.02	0.07	MoO3	0.10	0.1
48 Cd	k	0.22	10.11	0.06	0.05	CdO	0.25	0.2
53 I	k	6.08	20.15	1.55	0.46	I2O5	8.00	3.4
82 Pb	L	0.03	28.31	0.00	0.01	PbO	0.03	0.0
O		29.62	14.63	59.76				





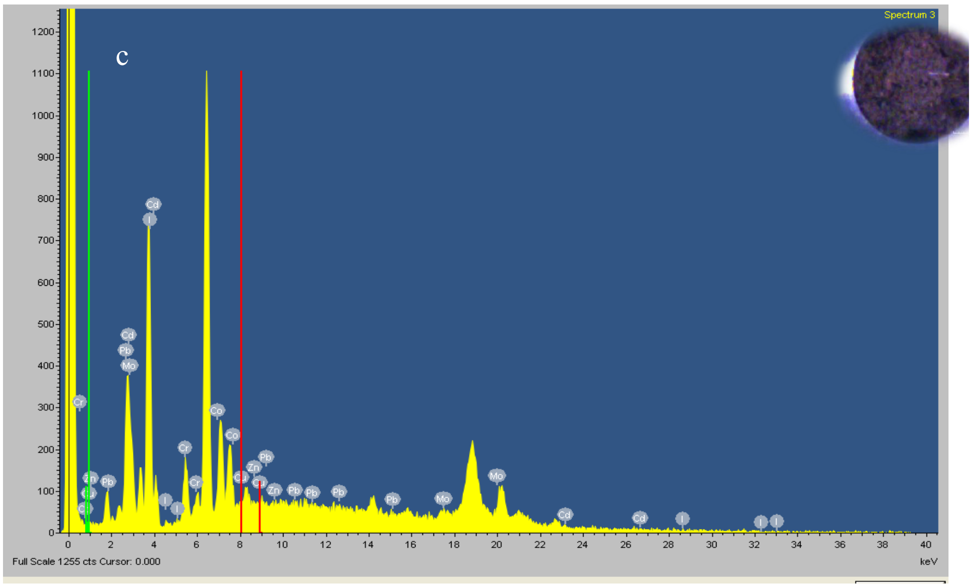


Fig. 1. EDRF analysis of represented leaf samples collected from (a) HPA (traffic area), (b) LPA (industrial area) and (c) Control area (botanical garden).

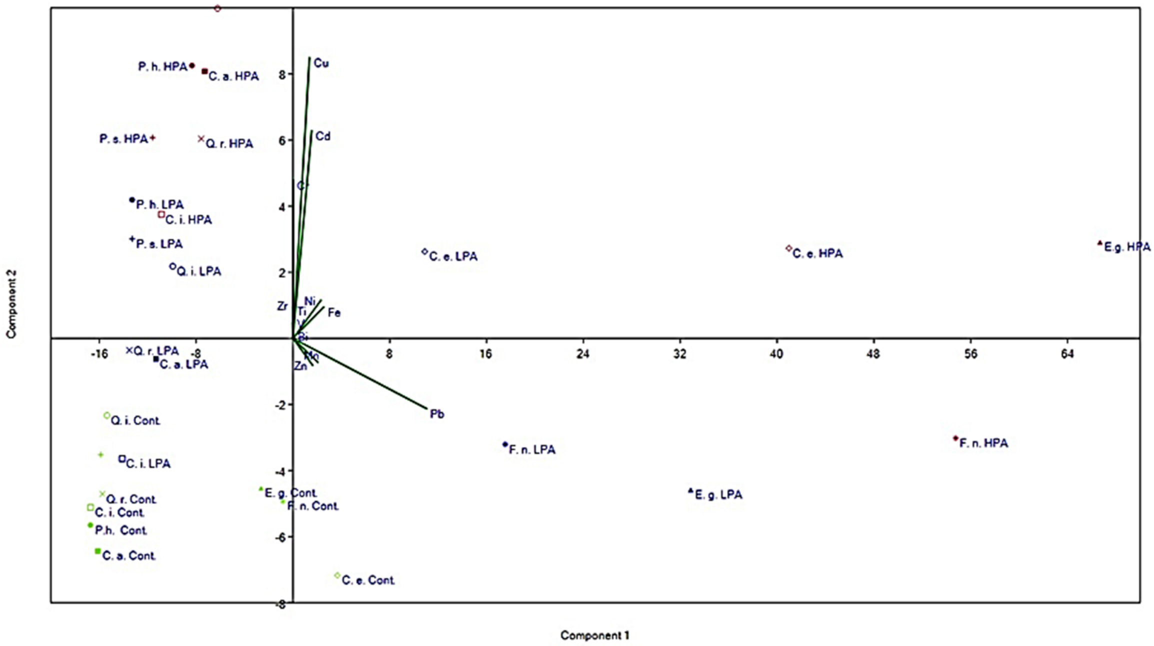


Fig. 2. Principle component analysis of digested leaves sample data set against heavy metals accumulation level.

Conclusions

The findings of this research indicate that in the background region the mean metal content was smaller than in the other regions, whereas in the HPA (traffic zone) and LPA (industrial region) the largest metal content was recorded. The largest and lowest mean metal content in the plant leaves were as follows: in the *Eucalyptus globules* and *Q. ilex* leaves, the highest Cu content was noted, the highest concentrations of Zn were observed in *E. globulus* and *F. nitida* leaves, the highest concentrations of Pb and Cd were observed in *Eucalyptus globules* and Q. robur leaves, and the lowest concentrations of all heavy metals were found mainly in the leaves of *Cupressusarizoneka* and *Cupressusitalica*. In some plant species under test, the metal content was below the toxicity levels in plants such as V ; Ni ; Ti ; Mn and Bi, while other metals exceeded the normal toxicity range such as Cu, Pb, Fe, Cr and Cd. Based on the present results, *E. globules*, *casuarinas equisetifolia* and *F. nitida* were effective for sequestering Cu, Cd, Cr, Fe and Pb pollution, while *P. halepensis*, *P. sylvestris, C. arizoneka* and *Q. robur* are hyper accumulators and effective for decreasing V, Ti, Zr and Bi pollution. Meanwhile, based on previous results, *Eucalyptus globules*, *Q. ilex*, *F. nitida* and *Q. robur* might be recommended for planting in most polluted areas in Baku.

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