Urban Forestry & Urban Greening 65 (2021) 127359

Contents lists available at ScienceDirect

Urban Forestry & Urban Greening

journal homepage: www.elsevier.com/locate/ufug

Similarities and differences of potentially toxic elements contents in leaves of *Fraxinus excelsior* L. and *Platanus orientalis* L. in an urban environment

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ARTICLE INFO

Handling Editor: Francesco Ferrini

Keywords:
Pollution mitigation
Toxic elements
Urban environment

ABSTRACT

The recognition of the features and capabilities of potentially toxic elements (PTE) uptake from urban tree leaves is crucial for mitigating pollution and optimizing the allocation of green infrastructures of an urban environment. Therefore, Pb, Ni, Mo, Cu, Zn contents and spatiotemporal variation were investigated in the leaves of the most widespread urban trees in Yerevan (Armenia) (*Fraxinus excelsior* L. and *Platanus orientalis* L.) by means of a chemical approach based on atomic-absorption spectroscopy, after having washed them. The obtained results showed similarities in leaves Ni, Cu, Pb and Mo uptake. Meanwhile, only biologically non-essential elements (Mo and Pb) tend to accumulate in leaves during the vegetation season. This allows for the identification of localized pollution sources. Spatiotemporal variation of Zn contents suggested that *P. orientalis* L. is the less efficient tree species in Zn uptake. The study of the relationship of Pb, Ni, Mo, Cu, and land use by means of clr-biplots showed the absence of any potential links. Moreover, it was revealed that the element contents of leaves in green areas are similar to those observed in industrial and residential sites. The latter highlighted the need for the expansion of green areas with the use of scientifically justified species as a means of nature-based solution for pollution mitigation and better urban environmental management.

1. Introduction

The green infrastructure of urban areas plays a pivotal role in the formation of the city environment and its qualitative features, as well as it demonstrates a crucial ecological and aesthetic significance leading to the expansion of urban ecosystem services worldwide (ConnectingNature, 2020; Rocha et al., 2015).

At the same time, urban areas are projected to accommodate the 68 % of the world's population by 2050, and built-up areas have expanded to some 500,000 km^2 at the expense of green urban infrastructures (Nations, 2018; Sawidis et al., 2011). This will undoubtedly lead to the uncontrolled increase of pollutants (Solgi et al., 2020) and will cause harmful consequences for the overall ecosystem and human health (Calfapietra et al., 2015; Sanesi et al., 2007).

Trees constitute the main parts of the green urban infrastructure and ecosystem and improve the quality of urban environments (Liang et al., 2017; Patel et al., 2015). They deliver a number of environmental ecosystem services (EES): to name a few, amelioration of air quality, restoration of soil and water, amelioration of the microclimate, removal of CO_2 from the air, provision of habitat for biodiversity, support for resilient urban ecosystems, provision of genetic diversity, energy, nutrients and grey infrastructure resilience (Calfapietra et al., 2015; Roeland et al., 2019).

Among the pollutants of urban areas, potentially toxic elements (PTE) require special attention. These elements are ubiquitous, mainly non-biodegradable and hard for microorganisms to counter their toxic effect. Moreover, PTE migration, biodegradation, as well as accumulation in living organisms varies significantly. There are also huge differences in PTE sources in urban environment (Dadea et al., 2017; Dogan et al., 2014; Kabata-Pendias and Pendias, 2011). Interestingly, PTE emitted from different anthropogenic sources are transported in the atmosphere as aerosols, gases and particulates. Volatile metal(oid)s (i.e. arsenic (As), antimony (Sb), mercury (Hg) etc.) can be carried both as enriched constitution in particles and in gaseous form, while copper

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https://doi.org/10.1016/j.ufug.2021.127359
Received 15 September 2020; Received in revised form 21 August 2021; Accepted 21 September 2021

(Cu), lead (Pb), and zinc (Zn) are only transported bound to the particles, especially fine particulate matter (PM) (Bradl, 2005). These particles then deposit on soil, plants, as well as on tree leaf surfaces, serving as an essential source of PTE in soil and plants. For instance, it is known that for Pb more than 90 % of plant uptake is generated from atmospheric sources (Bradl, 2005), thus indicating that Pb contents in leaves may be a suitable means for the biomonitoring of air pollution by Pb.

The uptake and accumulation of PTE from atmospheric sources in plants can indeed follow three main pathways. Metals detected in the leaves can come from the soil, via uptake by plant roots (Tangahu et al., 2011) and be translocated through the xylem. The rate of PTE movement among tissues varies greatly, depending on the plant organ, its age, and the element involved (Dalenberg and Van Driel, 1990; Sawidis et al., 2011). At the same time, toxic elements deposit on leaves *via* wet and dry atmospheric deposition, and then they can remain on the surface or enter the leaf tissues (Kabata-Pendias and Pendias, 2011). When PTE are in gaseous form or bound to fine PM particles (i.e. smaller than 1 um), a high proportion of toxic elements may enter plant tissues via leaf cuticle and stomatal pores penetration and accumulate in the foliage (Aksoy and Demirezen, 2006). Since this foliar uptake from air is mainly governed by gas exchange (Beckett et al., 2000), it can thus vary depending on site conditions, tree species and seasonal variation (Liu et al., 2013), since stomatal conductance and related biochemical processes in leaf tissues are strongly temperature dependent (Shahid et al., 2017; Urban et al., 2017). Finally, when PTE are bound to coarse PM particles, they accumulate on the leaf surfaces, with a load that depends on the leaf morphological structures (such as leaf surface roughness, trichomes and stomata) and, thus, on the plant species (Sgrigna et al., 2020).

Several approaches have been proposed to characterize the PTE content of leaves, with the final goals of estimating the tree capacity in terms of air pollution mitigation and using tree leaves as passive filters for air quality biomonitoring. Some of these approaches focused on the PTE contained in coarse particles and accumulated on leaf surfaces, to ensure that all the analyzed material originated from air pollution. This can be obtained either by washing the leaves and then collecting the PM particles washed out on filters to be further analyzed (Kardel et al., 2020, 2018; Sgrigna et al., 2016) or by analyzing directly the PM particles on the leaf surfaces (Baldacchini et al., 2019, 2017; Castanheiro et al., 2020; Weerakkody et al., 2018). However, when these approaches were compared with chemical or magnetical analysis of the whole leaf materials, it was found that information on the real PTE uptake of trees could be lost (Castanheiro et al., 2020; Kardel et al., 2018). Additionally, site and tree species are also important factors conditioning atmospheric PTE depositions (Baldacchini et al., 2017; Kardel et al., 2018).

In this study, we focused on the characterization of PTE up-taken by *F. excelsior* L. and *P. orientalis* L. leaves investigating the contents of selected PTE (Pb, Ni, Mo), Cu, Zn), the seasonal variation of the content of tree leaf elements, and the possible link between element contents and the spatial location of trees. These will allow to reveal the related features of *F. excelsior* L. and *P. orientalis* L. under the specific natural climatic conditions and the ecological stress of Yerevan (Armenia), and establish a scientifically grounded basis for supporting the city municipality in decision making and in reasonable management of planting of studied tree species quantity within the city territory.

2. Materials and methods

2.1. Study site

Armenia's capital Yerevan has a strongly dissected relief which largely influences the local climate. The city enjoys a sharply continental climate: long warm summers, short cold winters, short springs and long falls. The average annual precipitation ranges from 250 to 370 mm (SCRA, 2019). The territory of the city is characterized by a high, steadily increasing level of traffic related dust load (Maghakyan et al., 2017), and by the presence of the plant of "Pure Iron" producing Ferromolybdenum and metal Mo, which is located in the southern part of the city and was identified to be the dominant Mo pollution source (Tepanosyan et al., 2016). For many decades, PTEs have been the dominant pollutants of all environmental compartments of the city (Saghatelyan, 2004; Sahakyan, 2006; Tepanosyan et al., 2017, 2016). Additionally, during the last decades massive tree cutting and chaotic construction throughout Yerevan resulted in the reduction of green public areas. Simultaneously, the loss of some tree species and worsening of the condition of others (Hovhannisyan and Nersisyan, 2017) have clearly highlighted the need of targeted tree planting in the city territory.

2.2. Tree leaves sampling

Fraxinus excelsior L. (*F. excelsior* L.) and *Platanus orientalis* L. (*P. orientalis* L.) are among the most common widespread tree species planted in the parks and streets of Yerevan, which are native deciduous tree species (Hovhannisyan and Nersisyan, 2017), characterized as drought resistant and ecologically tolerant (Roloff et al., 2009), and have sufficiently high phyto-filtration potential (Nersisyan and Hovhannisyan, 2014). Therefore, *F. excelsior* L. and *P. orientalis* L. leaves were sampled in May and September 2015 from 20 and 13 sampling sites (Fig. 1) respectively, characterized by different land use (i.e., green, industrial or residential areas). In each sampling location, leaves were collected from four trees per species (biological replications), at 1.5–1.7 m above the ground level. The distance between the sampled trees was 5–7 m, depending on the number of trees at the single location. Leaves collected from each tree were without damages (dried-out branches, crown, and trunk deformation) or diseases. From each sampled tree, 25–30 leaves were selected. All the leaves collected from the same tree were stored in a paper bag immediately after sampling, labeled and then transported to the Central Analytical Laboratory of the Center for Ecological-Noosphere Studies (CENS) NAS Armenia.

2.3. Analytical methods

In order to determine the PTE contents of leaves, the dry ashing method was applied. The samples were washed with distilled water, chopped into small pieces, air dried at room temperature and weighted. The digestion of the samples was done according to the procedure described in the Analytical methods for AAS, 2000) publication. The subsamples of 0.5–2.0 g (depending on the expected contents of the elements to be determined) of the dry plant material were ground in a laboratory mill and 0.5–1.0 g of milled dried plant sample was placed in a porcelain crucible. Then, the porcelain crucible was placed in a cool muffle furnace and the samples were ashed at 500 °C overnight. The ash residues were cooled down to room temperature and dissolved in 5 mL of 20 % HCl. The obtained solution was filtered through acid-washed filter paper into a 50-mL volumetric flask, diluted with distilled water and mixed. The contents of the Pb, Ni, Mo, Cu, and Zn were measured through the atomic-absorption spectroscopy by AAnalyst 800 (Perkin Elmer, USA). All findings were calculated on dry weight basis (mg/kg^{-1} dry weight). The recovery of the analysis ranges between 96.6–116.5 % and RSD of duplicated samples: 2.75–7.06 %.

2.4. Data treatment and mapping

The descriptive statistics of *F. excelsior* L. and *P. orientalis* L. leaf PTE contents were calculated (Table 1) using SPSS20 software. The Shapiro-Wilk test was applied to check the normality of data distribution. The tests for the comparison of PTE contents for four cases of two groups of data (same species different season, same season different species) were performed based on the recommendations provided in Reimann et al. (2008) and the fact that the sample number of *F. excelsior* L. and *P. orientalis* L. was different. The comparison of PTE contents collected in different seasons was done using the paired T-test (for Pb, Ni, Cu, and

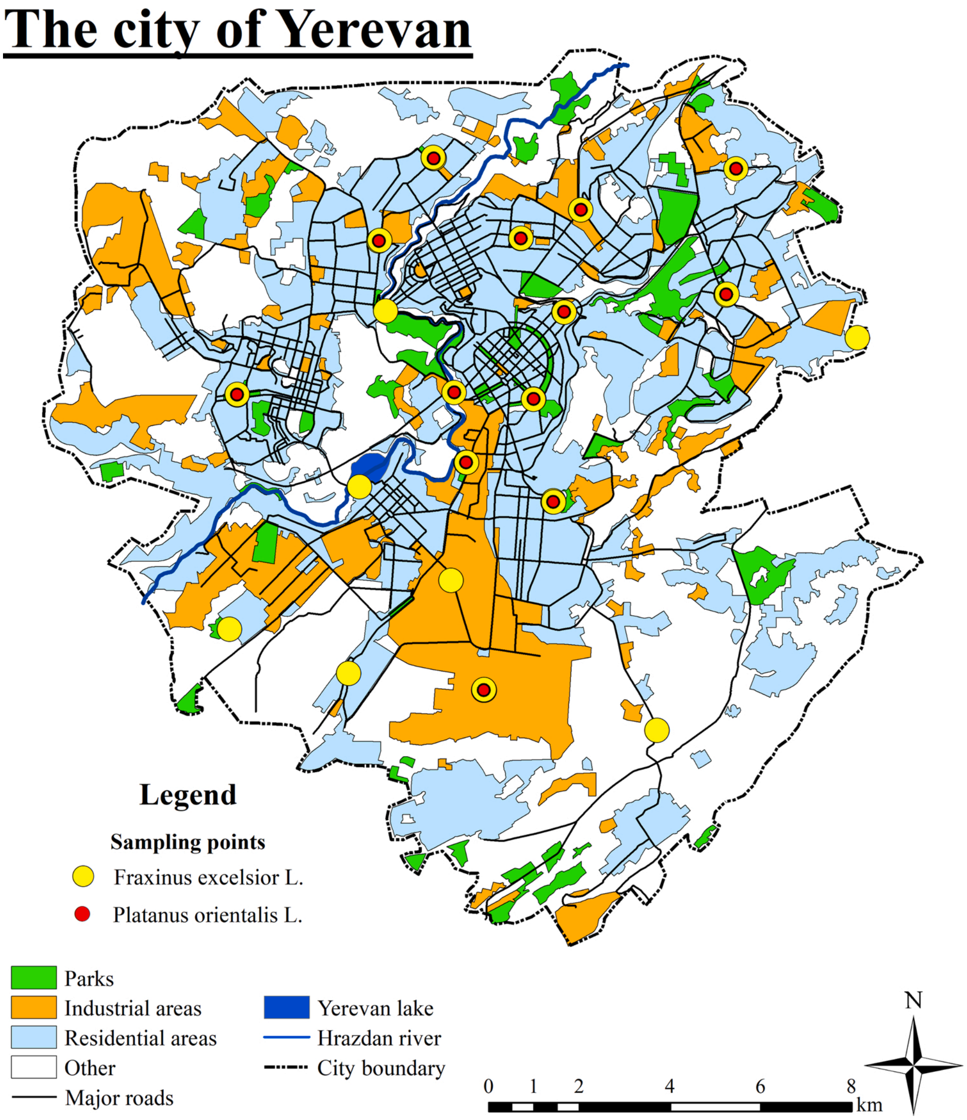

Fig. 1. Spatial distribution of sampling sites across the city of Yerevan.

Zn) and the Wilcoxon test (for Mo) while to compare PTE contents in different tree species, a two sample T-test (for Pb, Ni, Cu, and Zn) and the Mann Whitney *U* test (for Mo) were used. To study the relationship between the studied PTEs, compositional biplots of centered log-ratio (clr) transformed data were created (clr-biplot) (Fig. 5) after the identification of multivariate outliers through the application of the Atipicality index. The biplots were created using clr as transformation because it was an accepted method for opening a data set which treated the parts of composition symmetrically and kept the direct link to the variables (Reimann et al., 2008; RGSCoDa and CDA, 2017; Somma et al., 2021).

3. Results

3.1. Data analysis and contents of PTE in tree leaves

The descriptive statistics of the PTE contents in *F. excelsior* L. and *P. orientalis* L. leaves, as collected in two different seasons (i.e., May and September), is shown in Table 1. Table 1 demonstrates that in all cases the mean contents of the studied elements has decreased in the following order: Zn-Cu-Ni-Mo-Pb. The comparison of the mean contents of the studied tree leaves with the findings in the published literature showed that similar cases appeared to be just a few. Particularly, Monfared et al. (2013) studied the contents of Pb in *P. orientalis* L. leaves collected in October in Karaj city and reported a mean Pb content of 14.4 mg/kg which was 22.1 times greater than the mean Pb content of *P. orientalis* L. leaves observed in September of the same year. The possible explanation of such a high difference can be the fact that Monfared et al. (2013) collected their samples from an area with the highest traffic rate. In another study (Solgi et al., 2020) the mean contents of Cu (15.2 mg/kg), Zn (41.8 mg/kg), and Pb (51.4 mg/kg) in *F. excelsior* L. leaves collected in Bojnourd city in October were 1.5, 2.3, and 65.1 times greater than those contents observed in this study, respectively. In this case also, the Solgi et al. (2020) reported that the source of Cu, Zn, and Pb in *F. excelsior* L. leaves was the traffic density in the urban center district.

For *F. excelsior* L., the differences between the mean values of studied elements in May and September are different (>1.1) in the case of the contents of Pb, Mo, and Cu. Particularly, in May, the mean value of Cu is 1.3 times greater than in September whereas, compared with May, the mean values of Pb and Mo are 2.7 and 1.5 times greater in September, respectively. Additionally, Pb, Mo, and Cu show a relatively higher values of the coefficient of variation (CV) compared to other studied PTEs in both seasons. In particular, Mo is the element showing a higher value of CV: 188.5 % in May and 144 % in September. In the case of *P. orientalis* L. differences of studied PTE contents are observed for the Pb, Mo and Zn. As for the *F. excelsior* L., the higher mean contents of Pb

Table 1
Descriptive statistics of studied PTE contents (mg/kg) in leaves.

Elements	Sample number	Mean	Median	SEM	Skew.	Min	Max	CV, %
2015 May *F. excelsior L.*								
Pb	20	0.338	0.290	0.073	3.02	0.070	1.57	97.5
Ni	20	2.11	1.98	0.087	0.257	1.42	2.78	18.5
Mo	20	1.08	0.490	0.455	4.33	0.282	9.65	188
Cu	20	13.20	13.3	1.07	0.480	6.25	25.0	36.4
Zn	20	19.0	19.3	1.57	0.716	9.78	35.2	37.0
2015 September *F. excelsior L.*								
Pb	20	0.787	0.712	0.078	1.00	0.251	1.69	44.2
Ni	20	1.95	1.78	0.168	1.57	1.15	3.99	38.6
Mo	20	1.61	1.06	0.518	4.33	0.572	11.3	144
Cu	20	9.91	6.97	2.09	2.63	1.56	42.3	94.3
Zn	20	18.4	18.5	1.24	0.204	10.2	27.7	30.3
2015 May_*P. orientalis L.*								
Pb	13	0.302	0.296	0.026	0.680	0.168	0.484	31.3
Ni	13	2.38	2.28	0.177	0.597	1.61	3.61	26.8
Mo	13	1.38	0.554	0.735	3.52	0.310	10.1	192
Cu	13	11.9	12.5	0.882	0.124	7.50	18.1	26.7
Zn	13	19.9	20.4	1.62	0.352	11.1	31.5	29.3
2015 September *P. orientalis L.*								
Pb	13	0.646	0.602	0.085	1.39	0.283	1.44	47.7
Ni	13	2.30	2.18	0.265	1.37	1.22	4.28	41.5
Mo	13	2.18	1.09	0.891	3.32	0.787	12.6	147
Cu	13	13.4	8.33	2.94	1.90	5.50	42.2	79.2
Zn	13	15.0	15.3	0.938	0.064	8.52	22.3	22.5

and Mo are observed in September, exceeding the May results by 2.0 and 1.6 times, respectively.

In the case of Zn, a higher mean value is detected in May, and this exceeds the September mean value by 1.3 times. Again, the higher value of CV is observed in both cases for Mo, standing at 192 % and 147 % in May and September respectively. This indicates that in some of studied locations the Mo contents of both *F. excelsior* L. and *P. orientalis* L. leaves may have an anthropogenic origin. Indeed, CV values higher than 100 % mainly indicate anomalous contents of elements in the statistical sample (Johnson et al., 2011), and this could be due to the fact that the Mo leaf content is significantly higher at the sites close to the known anthropogenic sources compared to the other sites. This is further confirmed by the comparison of mean and median values of the tree leaf Mo content. Moreover, the value of skewness suggests the right skewed distribution of Mo, which indicates the deviation from the normal distribution and the presence of outliers and extreme values.

The Shapiro-Wilk test of normality and histograms (Fig. 2) shows that in all the studied cases the PTE content displays normal or lognormal distribution, besides Mo, which displays outliers and especially extreme values, for both species in both seasons. This is likely due to the sampling site being located very close to the anthropogenic sources of the Mo pollution, as suggested above.

In Fig. 3, the boxplots of the distributions of studied PTE contents are presented. It is evident that not only Mo but also other studied PTE display outliers and extreme values. Particularly, the Pb content of *F. excelsior* L. leaves shows one positive outlier and extreme value in May and two positive outliers in September, while for the Pb content of *P. orientalis* L. leaves two positive outliers are detected both in May and September. In the case of Ni, a single positive outlier and an extreme value for *F. excelsior* L., as well as two positive outliers for *P. orientalis* L., are observed in September.

The Mo content of *F. excelsior* L. leaves displays a single positive extreme value and a single positive outlier and extreme value, in May and September, respectively. In the case of *P. orientalis* L., a single positive outlier, an extreme value and two positive extreme values are observed, in May and September, correspondingly. For the Cu content, a single positive outlier and two extreme values are detected in the leaves of *F. excelsior* L. collected in September, whereas a single positive outlier is observed in the case of *P. orientalis* L. leaves collected in September. Among all the studied PTE, Zn showed the lowest number of outliers and extreme values. In particular, a single positive outlier and a single negative outlier are observed in *P. orientalis* L. leaves collected in September.

Fig. 4 demonstrates the spatial distribution of the observed outliers and extreme values of the contents of the studied elements in the city territory. The detected outliers and extreme values of the studied PTE contents in leaves are observed in trees which are spatially located in the areas where residential and industrial land use is dominant. However, it is worth noting that the detailed examination of studied PTE outliers and extreme values show that, while in the case of *F. excelsior* L. (Fig. 4a) the outliers and extreme values are spatially located all over the city except its central and eastern areas, for the *P. orientalis* L. (Fig. 4b) a spatial cluster of outliers and extreme values is observed in the northeastern area of the city. There are only two sampling sites where both species display outliers and extreme values: one is located in the southern industrial area of the city (elements: Pb and Mo) and the other - in the northern part situated on the border of residential and industrial areas (elements: Cu). The sampling site where Mo and Pb outliers and extreme values have been detected are spatially located near the plant of “Pure Iron” producing Ferromolybdenum and metal Mo. It needs to be mentioned that at this site extremely high contents of these elements have been observed in soil (Tepanosyan et al., 2017, 2016) and leaves dust deposition too (Maghakyan et al., 2016; Saghatelyan et al., 2014).

The paired *t*-test was then applied, in order to understand if Pb, Ni, Cu, and Zn contents in leaves of the same tree species sampled in different seasons can be considered equal. In the case of Mo, the non-parametric version of the paired *t*-test, the Wilcoxon test, was applied. For both species, the output of both tests indicated that the content of Ni and Cu in the leaves can be considered equal in the two seasons, while the content of Pb and Mo is significantly different, increasing from May to September, for both species. It is known that Ni and Cu are essential elements for plants and play an important role in their metabolism (Kabata-Pendias and Pendias, 2011). These elements are actively used in plants nutrition and their contents in leaves should decrease at the end of vegetation. Conversely, in our case, Ni and Cu leaf content does not differ significantly during the studied seasons, indicating the possibility of anthropogenic emissions (likely, traffic related (Sgrigna et al., 2016), which induce the absorption of these elements by plants, compensating their internal use. For Pb and Mo, which have been previously reported to be the main urban pollutants of Yerevan (Maghakyan et al., 2016; Saghatelyan et al., 2014; Tepanosyan et al., 2017, 2016), accumulation in leaf tissues during the vegetation period is expected and, indeed,

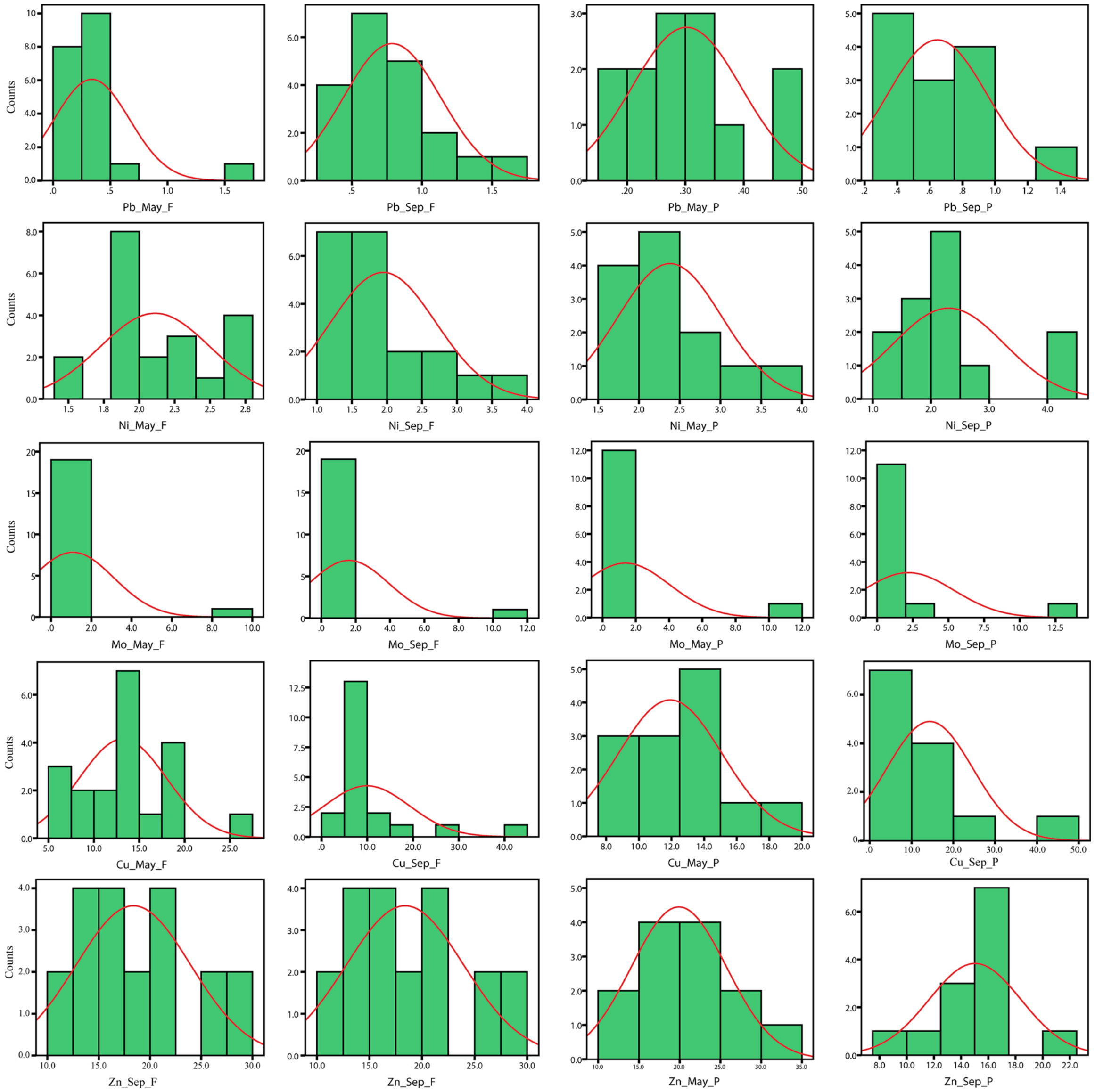

Fig. 2. Distribution of the observed leaf PTE concentration (in mg/kg) over the sampled sites, for *Fraxinus excelsior* L. (*F*; 20 sampling sites) and *Platanus orientalis* L. (*P*; 13 sampling sites), as obtained by leaves collected in May and September 2015 in Yerevan (Armenia). The superimposed red curves are the best fit of the histograms as obtained by using a Gaussian curve (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

observed, since their measured content increases from May to September. A different behavior is observed for the Zn contents in leaves, since it is not statistically different in the two seasons in the case of *F. excelsior* L., while it decreases with the vegetation period for *P. orientalis* L. Just like Ni and Cu, Zn too is an element which is used by plants, and thus its contents should decrease during the vegetation period. The obtained results suggest that the plant uptake is compensating the Zn use in the case of *F. excelsior* L., while it does not happen in *P. orientalis* L. This could relate to the features of PTE leaves uptake, since the rate of trace element movement among tissues varies greatly, depending on the plant organ, its age, and the element involved (Dalenberg and Van Driel, 1990; Kabata-Pendias and Pendias, 2011; Tangahu et al., 2011). In particular, just like Cu and Mo, Zn is absorbed actively which requires metabolic energy and takes place against a chemical gradient, while Pb and Ni are absorbed passively, in particular, through the non-metabolic circular penetration.

Finally, the comparison of the central values of the studied PTE contents in the two tree species in the same season was performed by using the two sample *t*-test and the Mann Whitney *U* test. The results show that for Pb, Ni, Cu and Mo contents of the central values of the distribution in the same season for both tree species are equal. Similar results have been obtained for another study (Monfared et al., 2013) investigating *P. orientalis* L. and *Fraxinus rotundifolia* shoots and leaves in October, in which the authors noted that the differences in contents of Pb among leaves of the species was not significant. On the other hand, while the same is observed also for the leaf Zn content of the two species in May, the central value of the Zn contents in September is significantly different. When combining this with what was observed for the seasonal variability of Zn contents in the leaves of the two species, this further suggested that a different uptake and metabolic processes occurred for Zn in the two species.

3.2. The relationship of studied PTE in tree leaves

The outputs of statistical tests performed in the previous section showed that for Pb, Ni, Cu and Mo results of two studied species for the same season displayed a similar sample distribution and central values. Therefore, in order to reveal the possible relationship between these

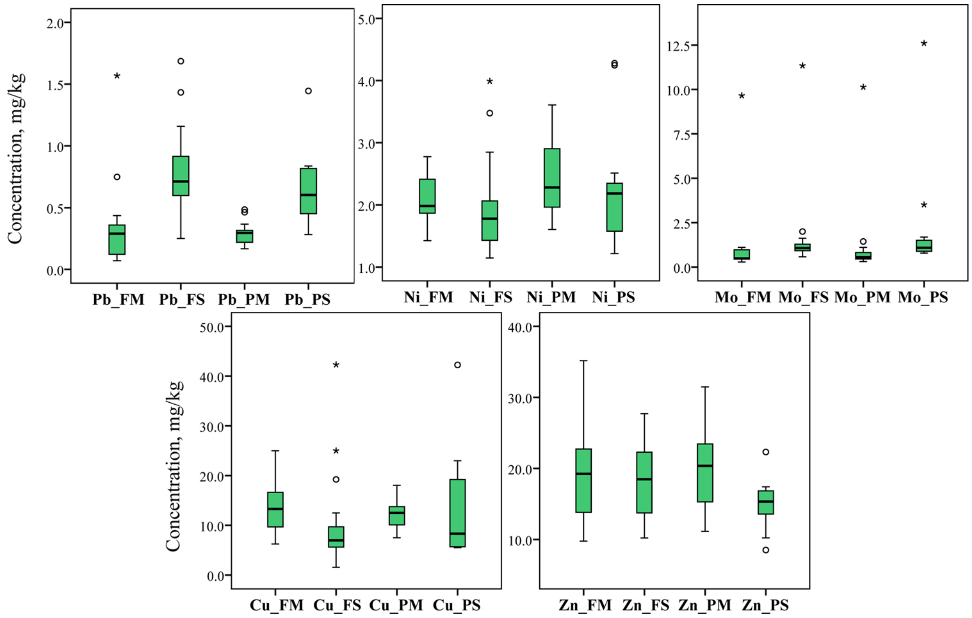

Fig. 3. Box-plots of the PTE concentration (mg/kg) in leaves of *Fraxinus excelsior* L. *(F)* and *Platanus orientalis* L.*(P)*, as collected in May (M) and September (S) 2015 in Yerevan (Armenia).

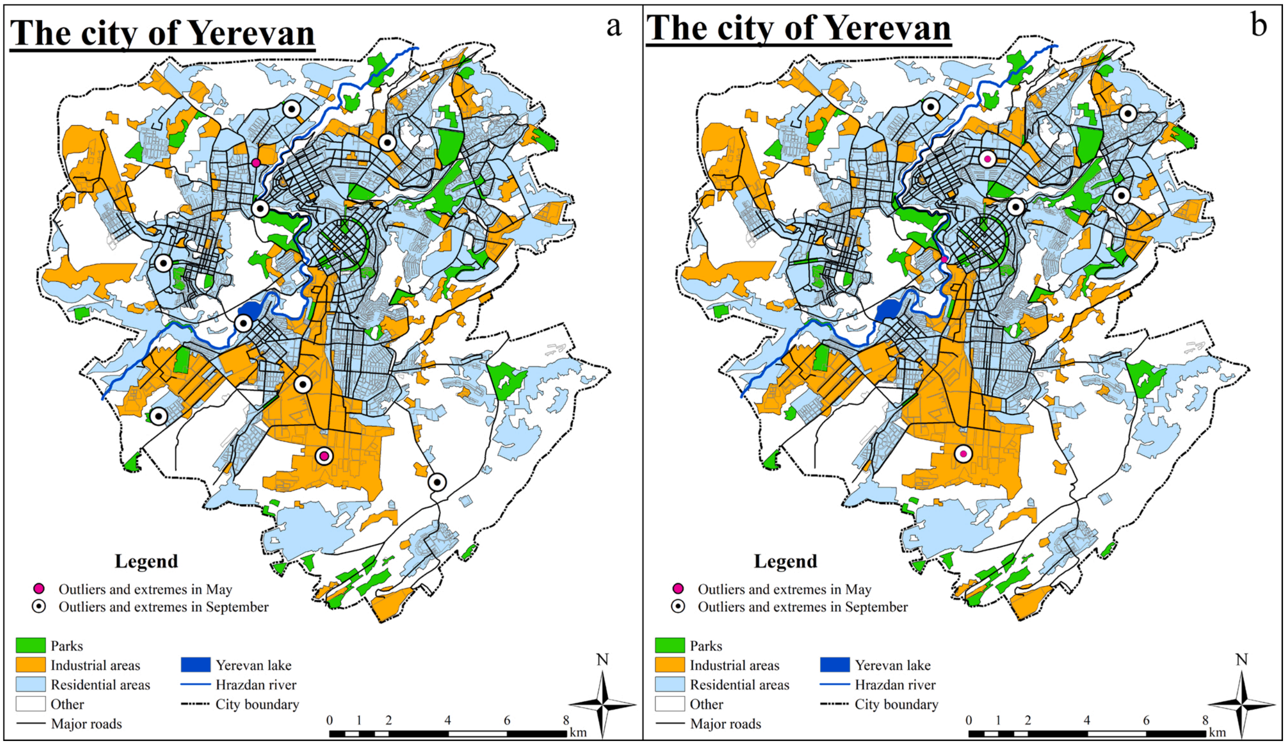

Fig. 4. Spatial distribution of the outliers and extremes values of PTE concentrations in leaves of Fraxinus excelsior L. (a) and Platanus orientalis L. (b), as collected in two different seasons (i.e., May and September 2015), per sampling site, in the city of Yerevan (Armenia).

elements, the datasets of *F. excelsior* L. and *P. orientalis* L. were combined, thus forming a dataset consisting of 33 samples. The combination of the dataset fulfilled the requirement of the sample number (n) vs a parameter (p) a ratio (Reimann et al., 2008) and allowed the creation of the compositional biplots of the clr-transformed data (clr-biplot) (Fig. 5). In addition, information on the dominant land use type was added to the clr-biplot, as represented by the colour of the observations, in order to reveal any possible links between the element contents and the land use in the sampling site. It needs to be mentioned that prior to the creation of clr-biplots, the multivariate outliers were detected through the application of Atipicality index and removed in order to exclude any possible bias linked to the theme.

The obtained clr-biplots explain the 85 % and 87 % of the total variability for May and September cases, respectively. However, no relationship is observed among the element contents in both seasons. Moreover, from the clr-biplots it is evident that there is no clear link between the sampling sites land use and the element contents. This may be explained by three main reasons: parks located in the city territory

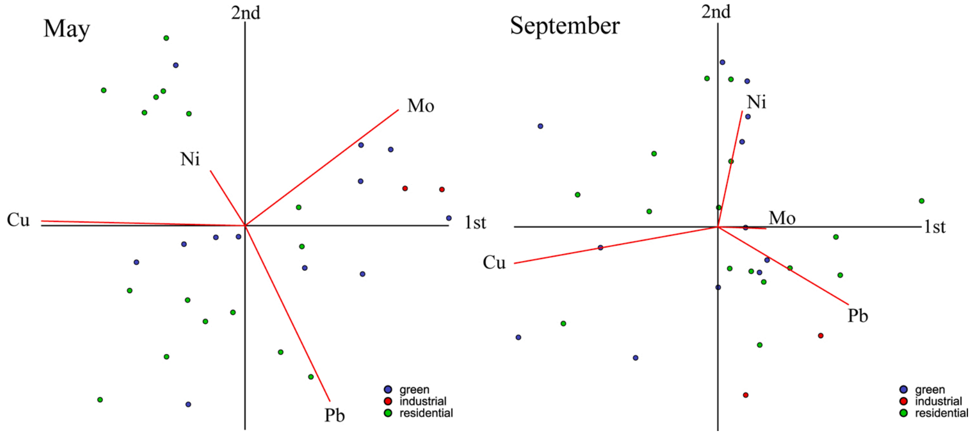

Fig. 5. Clr-biplots of the content of Pb, Ni, Cu and Mo in urban tree leaves collected in Yerevan (Armenia) in May and September.

are very small and exhibit the influence of closely located residential and industrial areas; emission from the iron plant is known to diffuse over the whole city territory (Tepanosyan et al., 2016); all sampling sites are close to the main roads of the city.

4. Conclusions

This study investigated the amounts and spatiotemporal variation of PTE (Pb, Ni, Mo, Cu, and Zn) in leaves of *F. excelsior* L. and *P. orientalis* L. growing in the urban environment of the city of Yerevan. Among all elements, only Mo distribution deviated from the normal standard for which a point source of pollution was identified. Moreover, statistically significant differences were observed for Mo contents in the studied seasons indicating its accumulation in leaf tissues during the vegetation period. The latter was observed for Pb contents, as well. This allows to suggest that in case of localized pollution sources, this methodology can provide information on the pollution source apportionment. The comparison of the studied PTE in two species allows concluding that different uptake and metabolic processes seem to be connected with Zn, while *P. orientalis* L. being the less efficient one in Zn uptake. At the same time, similar features in Ni, Cu, Pb and Mo uptake by leaves were observed. However, no relationship was identified between these PTE inferring that the four elements, even being diffused over the whole city territory, had different sources. The relationship between the elements and city land use was missing too. In particular, it was found that green areas did not differ from industrial and residential sites in terms of the elements contents and this reinforced the urgent necessity of improving the green areas in the city territory. This study indicated the need for thorough investigation of future details and incorporation of additional environmental media and tree parts such as soil and air dust in order to reveal the complex mechanism of PTE pathways, their accumulation features and behaviors in trees, as well as to provide scientifically grounded base to the city municipality for decision making and better urban environmental management.

Author contributions

Hovhannisyan H.: Investigation, Methodology, Writing - original draft.

Tepanosyan G.: Formal analysis, Visualization, Writing - Original Draft, Writing - Review & Editing.

Gevorgyan A.: Visualization, Writing - Original Draft, Writing - Review & Editing.

Baldacchini C.: Conceptualization, Writing - Original Draft, Writing - Review & Editing.

Sahakyan L.: Conceptualization, Data Curation, Writing - Original Draft, Writing - Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Aksoy, A., Demirezen, D., 2006. Fraxinus excelsior as a biomonitor of heavy metal pollution. Polish J. Environ. Stud. 15, 27–33.

Analytical methods for AAS, 2000. Analytical Methods for Atomic Absorption Spectrometry. PerkinElmer Instruments LLS.

Baldacchini, C., Castanheiro, A., Maghakyan, N., Sgrigna, G., Verhelst, J., Alonso, R., Amorim, J.H., Bellan, P., Bojović, D.D., Breuste, J., Bühler, O., Cântar, I.C., Cariñanos, P., Carriero, G., Churkina, G., Dinca, L., Esposito, R., Gawroński, S.W., Kern, M., Le Thiec, D., Moretti, M., Ningal, T., Rantzoudi, E.C., Sinjur, I., Stojanova, B., Aničić Urošević, M., Velikova, V., Živojinović, I., Sahakyan, L., Calfapietra, C., Samson, R., 2017. How Does the Amount and Composition of PM Deposited on Platanus acerifolia Leaves Change Across Different Cities in Europe? Environ. Sci. Technol. 51, 1147–1156. https://doi.org/10.1021/acs.est.6b04052.

Baldacchini, C., Sgrigna, G., Clarke, W., Tallis, M., Calfapietra, C., 2019. An ultra-spatially resolved method to quali-quantitative monitor particulate matter in urban environment. Environ. Sci. Pollut. Res. 26, 18719–18729. https://doi.org/10.1007/s11356-019-05160-8.

Beckett, K.P., Freer-Smith, P.H., Taylor, G., 2000. Particulate pollution capture by urban trees: effect of species and windspeed. Glob. Chang. Biol. 6, 995–1003. https://doi.org/10.1046/j.1365-2486.2000.00376.x.

Bradl, H.B., 2005. In: Heike, B. (Ed.), Heavy Metals in the Environment : [Origin, Interaction and Remediation]. Elsevier Academic Press.

Calfapietra, C., Peñuelas, J., Niinemets, Ü., 2015. Urban plant physiology: adaptation-mitigation strategies under permanent stress. Trends Plant Sci. 20, 72–75. https://doi.org/10.1016/j.tplants.2014.11.001.

Castanheiro, A., Hofman, J., Nuyts, G., Joosen, S., Spassov, S., Blust, R., Lenaerts, S., De Wael, K., Samson, R., 2020. Leaf accumulation of atmospheric dust: biomagnetic, morphological and elemental evaluation using SEM, ED-XRF and HR-ICP-MS. Atmos. Environ. 221, 117082 https://doi.org/10.1016/j.atmosenv.2019.117082.

ConnectingNature, 2020. Connecting Nature [WWW Document].

Dadea, C., Russo, A., Tagliavini, M., Mimmo, T., Zerbe, S., 2017. Tree species as tools for biomonitoring and phytoremediation in urban environments: a review with special regard to heavy metals. Arboric. Urban For. 43, 155–167.

Dalenberg, J.W., Van Driel, W., 1990. Contribution of atmospheric deposition to heavy-metal concentrations in field crops. Netherlands J. Agric. Sci. 38, 369–379.

Dogan, Y., Unver, M.C., Ugulu, I., Calis, M., Durkan, N., 2014. Heavy metal accumulation in the bark and leaves of juglans regia planted in artvin city, Turkey. Biotechnol. Biotechnol. Equip. 28, 643–649. https://doi.org/10.1080/13102818.2014.947076.

Hovhannisyan, H.A., Nersisyan, G.S., 2017. A complex approach to the development of green infrastructure of Armenia's cities. Procedia Environ. Sci. 37, 474–482. https://doi.org/10.1016/j.proenv.2017.03.020.

Johnson, C.C., Demetriades, A., Locutura, J., Ottesen, R.T., 2011. Mapping the Chemical Environment of Urban Areas. Wiley. https://doi.org/10.1017/CBO9781107415324.004.

Kabata-Pendias, A., Pendias, K., 2011. Trace Elements in Soils and Plants. Taylor & Francis Group, LLC.

Kardel, F., Wuyts, K., De Wael, K., Samson, R., 2018. Biomonitoring of atmospheric particulate pollution via chemical composition and magnetic properties of roadside tree leaves. Environ. Sci. Pollut. Res. 25, 25994–26004. https://doi.org/10.1007/s11356-018-2592-z.

Kardel, F., Wuyts, K., De Wael, K., Samson, R., 2020. Assessing atmospheric dry deposition via water-soluble ionic composition of roadside leaves. J. Environ. Sci.

Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 0, 1–9. https://doi.org/10.1080/10934529.2020.1752589.

Liang, J., Fang, H.L., Zhang, T.L., Wang, X.X., Liu, Y.D., 2017. Heavy metal in leaves of twelve plant species from seven different areas in Shanghai. China. Urban For. Urban Green. 27, 390–398. https://doi.org/10.1016/j.ufug.2017.03.006.

Liu, W., Ni, J., Zhou, Q., 2013. Uptake of heavy metals by trees: Prospects for phytoremediation. Mater. Sci. Forum 743–744, 768–781. https://doi.org/10.4028/www.scientific.net/MSF.743-744.768.

Maghakyan, N., Tepanosyan, G., Belyaeva, O., Sahakyan, L., Saghatelyan, A., 2016. Assessment of pollution levels and human health risk of heavy metals in dust deposited on Yerevan's tree leaves (Armenia). Acta Geochim. 1–11. https://doi.org/10.1007/s11631-016-0122-6.

Maghakyan, N., Tepanosyan, G., Belyaeva, O., Sahakyan, L., Saghatelyan, A., 2017. Assessment of pollution levels and human health risk of heavy metals in dust deposited on Yerevan's tree leaves (Armenia). Acta Geochim. 36, 16–26. https://doi.org/10.1007/s11631-016-0122-6.

Monfared, S.H., Matinizadeh, M., Shirvany, A., Amiri, G.Z., Fard, R.M., Rostami, F., 2013. Accumulation of heavy metal in Platanus orientalis, Robinia pseudoacacia and Fraxinus rotundifolia. J. For. Res. 24, 391–395. https://doi.org/10.1007/s11676-012-0313-x.

Nations, U., 2018. The world' s cities in 2018. World's Cities 2018 - Data Bookl. (ST/ESA/ SER.A/417) 34.

Nersisyan, G., Hovhannisyan, H., 2014. The impact of man-made pollution upon arboreous plants of Yerevan. Electron. J. Nat. Sci. NAS RA N 1 (22), 33–38.

Patel, K.S., Sharma, R., Dahariya, N.S., Yadav, A., Blazhev, B., Matini, L., Hoinkis, J., 2015. Heavy metal contamination of tree leaves. Am. J. Anal. Chem. 06, 687–693. https://doi.org/10.4236/ajac.2015.68066.

Reimann, C., Filzmoser, P., Garrett, R.G., Dutter, R., 2008. Statistical Data Analysis Explained. https://doi.org/10.1002/9780470987605.

RGSCoDa, R.Gin S., CDA, 2017. Compositional Data Analysis with CoDaPack and R..

Rocha, S.M., Zulian, G., Maes, J., Thijssen, M., 2015. Mapping and Assessment of Urban Ecosystems and Their Services. https://doi.org/10.2788/638737.

Roeland, S., Moretti, M., Amorim, J.H., Branquinho, C., Fares, S., Morelli, F., Niinemets, Ü., Paoletti, E., Pinho, P., Sgrigna, G., Stojanovski, V., Tiwary, A., Sicard, P., Calfapietra, C., 2019. Towards an integrative approach to evaluate the environmental ecosystem services provided by urban forest. J. For. Res. 30, 1981–1996. https://doi.org/10.1007/s11676-019-00916-x.

Roloff, A., Korn, S., Gillner, S., 2009. The Climate-Species-Matrix to select tree species for urban habitats considering climate change. Urban For. Urban Green. 8, 295–308. https://doi.org/10.1016/j.ufug.2009.08.002.

Saghatelyan, A.K., 2004. Peculiarities of Heavy Metal Distribution on the Territory of Armenia. CENS NAS RA, Yerevan.

Saghatelyan, A., Sahakyan, L., Belyaeva, O., Maghakyan, N., 2014. Studying atmospheric dust and heavy metals on urban sites through synchronous use of different methods. J. Atmos. Pollut. 2, 12–16. https://doi.org/10.12691/jap-2-1-3.

Sahakyan, L.V., 2006. The assessment of heavy metal stream in the air basin of Yerevan. Chin. J. Geochem. 25, 95–96. https://doi.org/10.1007/BF02839921.

Sanesi, G., Lafortezza, R., Marziliano, P.A., Ragazzi, A., Mariani, L., 2007. Assessing the current status of urban forest resources in the context of Parco Nord, Milan, Italy. Landsc. Ecol. Eng. 3, 187–198. https://doi.org/10.1007/s11355-007-0031-2.

Sawidis, T., Breuste, J., Mitrovic, M., Pavlovic, P., Tsigaridas, K., 2011. Trees as bioindicator of heavy metal pollution in three European cities. Environ. Pollut. 159, 3560–3570. https://doi.org/10.1016/j.envpol.2011.08.008.

SCRA, 2019. Statistical Yearbook of Armenia / Armenian Statistical Service of Republic of Armenia. National Statistical Service of the Republic of Armenia.

Sgrigna, G., Baldacchini, C., Esposito, R., Calandrelli, R., Tiwary, A., Calfapietra, C., 2016. Characterization of leaf-level particulate matter for an industrial city using electron microscopy and X-ray microanalysis. Sci. Total Environ. 548–549, 91–99. https://doi.org/10.1016/j.scitotenv.2016.01.057.

Sgrigna, G., Baldacchini, C., Dreveck, S., Cheng, Z., Calfapietra, C., 2020. Relationships between air particulate matter capture efficiency and leaf traits in twelve tree species from an Italian urban-industrial environment. Sci. Total Environ. 718, 137310 https://doi.org/10.1016/j.scitotenv.2020.137310.

Shahid, M., Dumat, C., Khalid, S., Schreck, E., Xiong, T., Niazi, N.K., 2017. Foliar heavy metal uptake, toxicity and detoxification in plants: a comparison of foliar and root metal uptake. J. Hazard. Mater. 325, 36–58. https://doi.org/10.1016/j.jhazmat.2016.11.063.

Solgi, E., Keramaty, M., Solgi, M., 2020. Biomonitoring of airborne Cu, Pb, and Zn in an urban area employing a broad leaved and a conifer tree species. J. Geochemical Explor. 208, 106400 https://doi.org/10.1016/j.gexplo.2019.106400.

Somma, R., Ebrahimi, P., Troise, C., De Natale, G., Guarino, A., Cicchella, D., Albanese, S., 2021. The first application of compositional data analysis (CoDA) in a multivariate perspective for detection of pollution source in sea sediments: the Pozzuoli Bay (Italy) case study. Chemosphere 274, 129955. https://doi.org/10.1016/j.chemosphere.2021.129955.

Tangahu, B.V., Sheikh Abdullah, S.R., Basri, H., Idris, M., Anuar, N., Mukhlisin, M., 2011. A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. Int. J. Chem. Eng. 2011 https://doi.org/10.1155/2011/939161.

Tepanosyan, G., Sahakyan, L., Belyaeva, O., Saghatelyan, A., 2016. Origin identification and potential ecological risk assessment of potentially toxic inorganic elements in the topsoil of the city of Yerevan, Armenia. J. Geochem. Explor. 167, 1–11. https://doi.org/10.1016/j.gexplo.2016.04.006.

Tepanosyan, G., Sahakyan, L., Belyaeva, O., Maghakyan, N., Saghatelyan, A., 2017. Human health risk assessment and riskiest heavy metal origin identification in urban soils of Yerevan, Armenia. Chemosphere 184, 1230–1240. https://doi.org/10.1016/j.chemosphere.2017.06.108.

Urban, J., Ingwers, M.W., McGuire, M.A., Teskey, R.O., 2017. Increase in leaf temperature opens stomata and decouples net photosynthesis from stomatal conductance in Pinus taeda and Populus deltoides x nigra. J. Exp. Bot. 68, 1757–1767. https://doi.org/10.1093/jxb/erx052.

Weerakkody, U., Dover, J.W., Mitchell, P., Reiling, K., 2018. Quantification of the traffic-generated particulate matter capture by plant species in a living wall and evaluation of the important leaf characteristics. Sci. Total Environ. 635, 1012–1024. https://doi.org/10.1016/j.scitotenv.2018.04.106.