

BIOINDICATION OF TRACE METAL POLLUTION IN THE ATMOSPHERE OF BAKU CITY USING *LIGUSTRUM JAPONICUM*, *OLEA EUROPEA*, AND *PYRACANTHA COCCINEA* LEAVES

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Abstract. The leaves of *Ligustrum japonicum* (Oleaceae), *Olea europaea* (Oleaceae), and *Pyracantha coccinea* (Rosaceae) were evaluated with the aim of using them as bioindicators for trace metal contamination in Baku city, Azerbaijan, one of the most highly polluted cities worldwide. These species of trees are the most abundant in urban and rural areas of Azerbaijan, because of high tolerance against climatic influences due to their modesty and adaptability. Concentrations of Cd, Cr, Cu, Fe, and Pb were determined in the leaves by AAS method. The samples were collected at three locations with different degrees of trace metal pollution (industrial, high traffic, and reference [botanical garden] site). The highest element concentrations were detected at sites of high traffic. Up to 70 times higher Pb concentrations could be found in the leaves of the trees that reflect the known Pb problem around Baku. The results presented give a first impression of a correlation between the degree of trace metal contamination in the environment and the trace metal concentration in the leaves of *L. japonicum* and *O. europaea*.

Keywords: air pollution, trace metals, environmental monitoring, leaves, bioindicators, Baku, Azerbaijan.

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Introduction

Air pollution is an offensive risk and can be a genuine health hazard to humans as well as to animals, plants, and microorganisms. Plant tissues have shown to behave as an effective indicator of atmospheric pollution (e.g. Markert *et al.* 2003; Wolterbeek *et al.* 2010). Vegetation is an acceptable indicator of pollution impact to its vicinity, because plants have the ability to accumulate or reject trace metals so that their metal levels correlate to those in the air. The effect observed is a time-averaged result, which will be – in most cases – more reliable than that obtained from direct determination of the pollutant concentrations in air for a short period. Hence, analyzing plant tissues can often produce better results in terms of sensitivity and reproducibility (Lau, Luk 2001). Some plant species are especially useful as biological indicators to assess

air pollution because of their global distribution (e.g. Kardel *et al.* 2010). A lot of plant species have already been applied as bioindicator species (Baycu *et al.* 2006; Celik *et al.* 2005; Fraenzle *et al.* 2012; Markert *et al.* 2003; 2008; Mingorance, Oliva 2006; Youssef 2012). The contaminants can deposit on and in the surface of leaves (Salma *et al.* 2001) and increase their harmful effects on human health (Temesi *et al.* 2003). Accumulation of heavy metals causes chronic damage to ecosystems and must be carefully observed and monitored taking into account uptake, movement, and effects of the contaminants on both the environment and its biota (Fraenzle *et al.* 2012; Markert *et al.* 2008; Mingorance, Oliva 2006; Morselli *et al.* 2004).

The aim of the present study is to investigate the pollution levels of Cd, Cr, Cu, Fe, and Pb using leaves of plant species, such as *Ligustrum japonicum*, *Olea*

europaea, and *Pyracantha coccinea* from three different sites in and around Baku (the capital of Azerbaijan). Baku has been discussed as one of the highest polluted cities of the world (Luck 2008), being polluted by emissions of oil drillings. Ismailov and Akhoun-Zade (1999) reported that especially during 1991–1994, serious environmental problems were caused by petrochemical industry, power plants, metallurgical, and building materials industries situated in Baku. Important contaminants have been hydrocarbons through 1,665,000 tons/y of emission from oil refineries in Baku. After Sawidis *et al.* (2011) the environmental lead pollution is directly related to the density of traffic. The main part of the total vehicle fleet up to 65% is located in the city of Baku, which significantly affects the ecological background of the city.

The results of this study should answer the scientific question whether plant leaves of *L. japonicum*, *O. europaea*, and *P. coccinea* can be used as bioindicators for environmental pollution observation and control in Baku city. The three species under investigation meet the requirements of bioindicators: wide distribution, high abundance, accumulation of pollutants, easy to collect, simple identification and cultivation, and analytical fitness. The studied elements are common pollutants in the air, especially in industrial cities as Baku characterized by large petroleum industry and by high density of traffic (Babayeva 2002). The results are especially of interest as preliminary baseline data for environmental air pollution of Baku derived from tree leaves.

1. Materials and methods

1.1. Sampling of plant leaves

Leaves of the evergreen trees *L. japonicum* (*Oleaceae*), *P. coccinea* (*Rosaceae*), and *O. europaea* (*Oleaceae*) were selected in three different areas in and around Baku (Fig. 1): (1) industrial zone of Baku (Absheron peninsula), (2) region of Baku airport with high traffic, and (3) botanical garden of Baku State University as reference site (10 km distance to pollution sources). From each sampling point, leaves of five trees per species (all in between 30 and 40 years) were taken from April to June 2012. Leaves of four different branches of each tree were sampled at a height of 1.5–2 m above the ground. From each branch three shoots were chosen. The sampling procedure followed the method after Sawidis *et al.* (2011). Care was given to avoid the collection of leaves characterized by insect infestation, presence of honeydew, bird dropping, pesticide treatment, chlorosis or necrosis, coarse, and anomalous dust cover. The collected leaves (about 30 g per sample) were placed in paper envelopes immediately after collection and dried in the laboratory.

1.2. Analytical procedure

After drying and homogenization, the samples were placed in polythene bags and stored in a refrigerator at 4 °C. One gram of each sample was digested in an open quartz tube and 10 ml of concentrated HNO₃ (Merck) was added to each sample and the mixture was left at room temperature overnight. In the further course, the

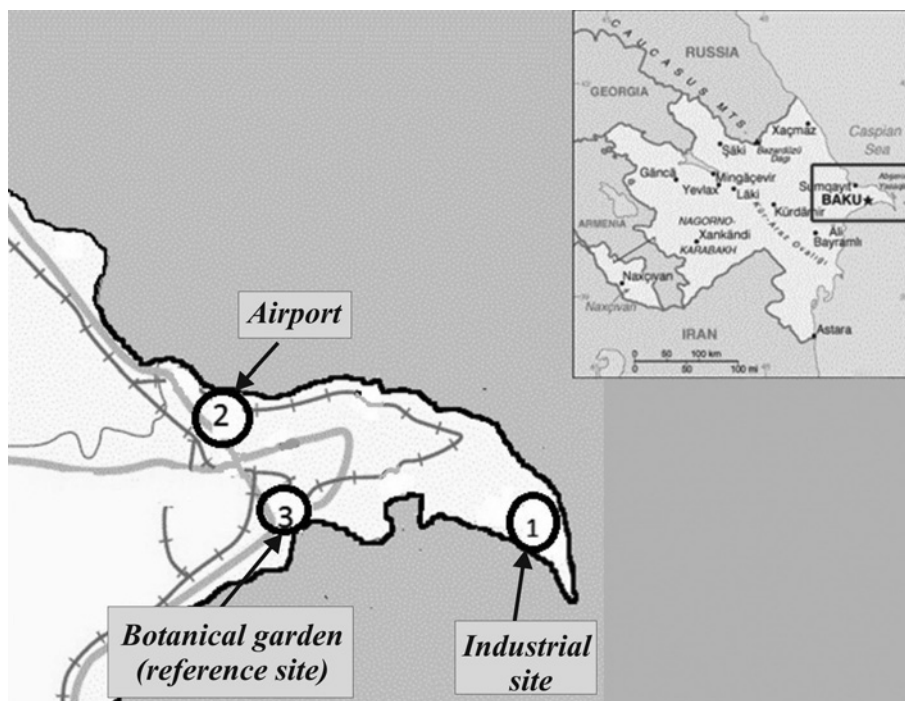


Fig. 1. Sampling locations of tree leaves in Baku, Azerbaijan

samples were heated at 50 °C for 2 h and subsequently heated at 160 °C for 4 h. The solution was filtered through a Whatman type 589/2 filter and the filtrate was diluted to 25 ml volume with double de-ionized water. These final solutions were analyzed for trace metal concentrations using an Atomic Absorption Spectrophotometer 850 (flame atomization, Perkin Elmer) at the Analysis Center of the Geological Institute at Azerbaijan, National Academy of Science. The quality controls of instrumental measurements were performed by using the National Standard of Azerbaijan BZ No.7–95, *O. europaea*. Statistical analyses were done by using Excel, Origin 6, and SPSS 11.5.

2. Results and discussion

The detected concentrations of Cd, Cr, Cu, Fe, and Pb in tree leaves from each sampling area are summarized in Table 1. Element specific concentrations are represented in Figures 2–6.

2.1. Cadmium

The leaves of *L. japonicum* showed the highest Cd amount up to 0.514 ± 0.13 ppm dry wt at site 2 in relation to the other tree species (traffic area, see Fig. 2). In general the Cd distribution pattern demonstrates higher Cd concentrations at the sampling sites 1 (industry) and 2 (traffic) in relation to the reference site (botanical garden). Compared to the average reference concentration for Cd in plants (0.03–0.5 ppm dry wt, Markert 1997) the Cd concentrations found do not cause pathological effects to plants.

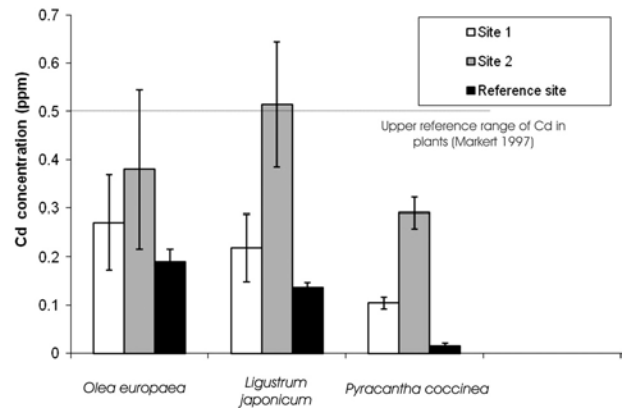


Fig. 2. Cadmium concentrations (ppm dry wt) in the leaves of *Olea europaea*, *Ligustrum japonicum*, and *Pyracantha coccinea* from different studied sites (site 1: industry; site 2: traffic; reference site: botanical garden)

2.2. Chromium

The leaves of *O. europaea* and *L. japonicum* represented much higher levels of 1.6–9 ppm dry wt in relation to the average reference concentration for Cr in plants (0.2–1 ppm dry wt, Markert 1997). However, the Cr concentrations in the leaves of *P. coccinea* taken from all three sampling sites matched the reference range of Cr contents in plants (up to 1 ppm dry wt).

2.3. Copper

The leaves of *O. europaea* showed the highest Cu amounts of up to 84 ppm dry wt at the sampling site 2 (traffic) and up to 73 ppm dry wt at sampling site 1 (industry) (Fig. 4). After Markert (1997) the average reference concentrations of Cu in plants differ between 2 and 20 mg/l. These values correspond with the Cu

Table 1. Comparison of Cd, Cr, Cu, Fe, and Pb concentrations in leaves of *Olea europaea*, *Ligustrum japonicum*, and *Pyracantha coccinea* from different studied sites

Plant species	Site	Cd, ppm \pm sd dry wt	Cr, ppm \pm sd dry wt	Cu, ppm \pm sd dry wt	Fe, ppm \pm sd dry wt	Pb, ppm \pm sd dry wt
<i>Olea europaea</i>	Site 1: industrial zone	0.27 ± 0.10	9 ± 3	73 ± 14	273 ± 86	221 ± 31
	Site 2: high traffic (airport)	0.38 ± 0.16	7 ± 2	84 ± 18	188 ± 55	282 ± 40
	Site 3: reference site, botanical garden	0.19 ± 0.03	4 ± 1	21 ± 4	165 ± 66	70 ± 13
<i>Ligustrum japonicum</i>	Site 1: industrial zone	0.22 ± 0.07	4 ± 0.70	33 ± 9	232 ± 55	257 ± 24
	Site 2: high traffic (airport)	0.54 ± 0.13	4 ± 1	45 ± 10	250 ± 33	341 ± 73
	Site 3: reference site, botanical garden	0.14 ± 0.01	1.63 ± 0.35	6 ± 1	170 ± 31	99 ± 19
<i>Pyracantha coccinea</i>	Site 1: industrial zone	0.10 ± 0.01	0.47 ± 0.15	14 ± 3	98 ± 24	60 ± 11
	Site 2: high traffic (airport)	0.29 ± 0.03	0.39 ± 0.13	21 ± 5	122 ± 19	106 ± 13
	Site 3: reference site, botanical garden	0.02 ± 0.01	0.23 ± 0.02	3 ± 0.79	135 ± 23	53 ± 9

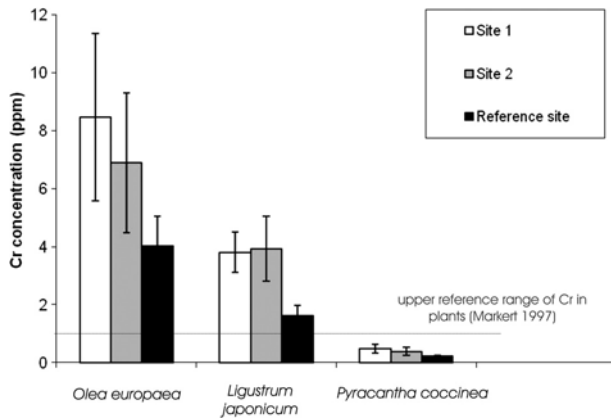


Fig. 3. Chromium concentrations (ppm dry wt) in the leaves of *Olea europaea*, *Ligustrum japonicum*, and *Pyracantha coccinea* from different studied sites (site 1: industry; site 2: traffic; reference site: botanical garden)

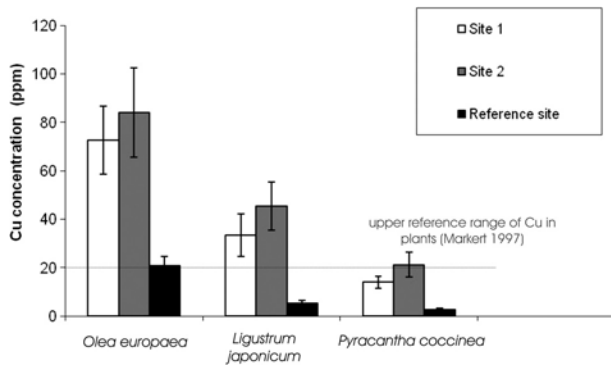


Fig. 4. Copper concentrations (ppm dry wt) in leaves of *Olea europaea*, *Ligustrum japonicum*, and *Pyracantha coccinea* from different studied sites (site 1: industry; site 2: traffic; reference site: botanical garden)

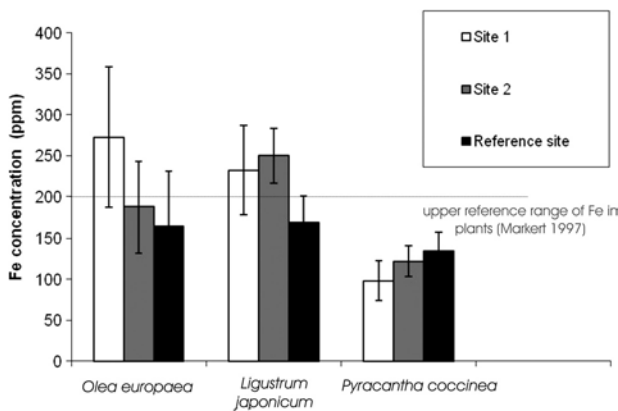


Fig. 5. Iron concentrations (ppm dry wt) in the leaves of *Olea europaea*, *Ligustrum japonicum*, and *Pyracantha coccinea* from different studied sites (site 1: industry; site 2: traffic; reference site: botanical garden)

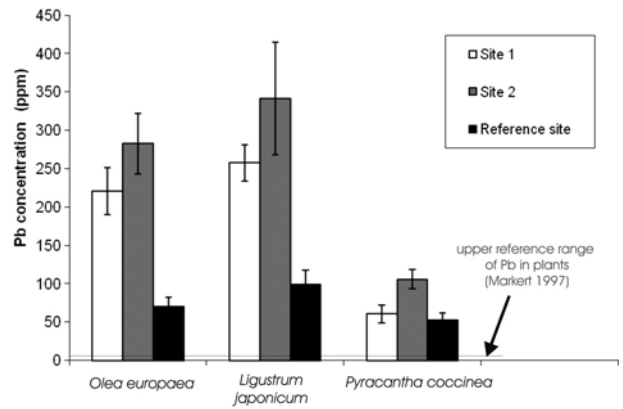


Fig. 6. Lead concentrations (ppm dry wt) in the leaves of *Olea europaea*, *Ligustrum japonicum*, and *Pyracantha coccinea* from different studied sites (site 1: industry; site 2: traffic; reference site: botanical garden)

concentrations evaluated in all three leaf species collected from the reference site (botanical garden; up to 21 ppm dry wt) and with the Cu concentrations measured in the leaves of *P. coccinea* at all studied places.

The Cu concentrations in the leaves of *O. europaea* and *L. japonicum* show up to four times higher Cu concentrations for the sampling points 1 and 2 compared to the “normal” values between 2 and 20 mg/l.

2.4. Iron

The leaves of *O. europaea* and *L. japonicum* showed higher Fe concentrations up to 273 ppm dry weight related to the leaves of *P. coccinea* (up to 135 ppm dry wt at the reference site, Fig. 5). According to Markert (1997) the average reference concentration for Fe in plants ranges from 5 to 200 ppm dry wt. These values corresponded with the Fe concentrations found in the leaves of *P. coccinea* at all samplings sites and with the Fe concentrations found in the leaves of *O. europaea* and *L. japonicum* collected from the reference site (botanical garden). The leaves of *O. europaea* taken from the sampling site no. 1 and the leaves of *L. japonicum* taken from the sampling sites 1 and 2 represented up to 30% higher Fe concentrations.

2.5. Lead

All evaluated Pb concentrations in the leaves of *O. europaea*, *L. japonicum*, and *P. coccinea* exceeded to a considerable degree the average reference concentration in plants of 0.1–5 ppm dry wt (Markert 1997). Figure 6 demonstrates that the Pb concentrations of the reference sites (botanical garden) were lower compared to site 1 (industry) and 2 (traffic). But these concentrations are much higher than the “normal” average value of 0.1–5 ppm dry wt given by Markert (1997). Values up to around 350 ppm dry wt in the

leaves of *L. japonicum* could be detected at the sampling site 2 (traffic). Figure 6 also demonstrates that the leaves of the tree species *O. europaea* and *L. japonicum* accumulate Pb in much higher concentrations compared to the leaves of *P. coccinea*.

2.6. Comparison of all chemical elements to each other

In summary, as expected, both sites (industry (1) and high traffic (2)) show higher element concentrations in comparison to the reference site (botanical garden site (3)). In case of Cd concentrations, all values measured at the sampling sites seem to be within a tolerable range. After Markert (1997) the average reference concentration of Cd in plants differs between 0.03 and 0.5 ppm dry wt. In the present study, the highest Cd concentration could be detected with 0.514 ppm dry wt in the leaves of *L. japonicum*. Based on these results, there is probably no significant Cd pollution in the urban region of Baku. The same could be found for Fe concentrations in the leaves studied. Related to the “normal” average reference concentration of Fe in plants after Markert (1997) with up to 200 ppm dry wt, the highest Fe concentration in the present study showed a value of 270 ppm dry wt. So the Fe concentrations in the leaves of the trees *O. europaea* and *L. japonicum* are slightly increased, but not significantly. The Fe concentrations in the leaves of *P. coccinea* are absolutely in an acceptable range.

For the elements Cr, Cu, and especially for Pb the situation is quite different. It is noticeable that the Cr and Cu concentrations in the leaves of *P. coccinea* are quite acceptable according to all studied places. Related to the Cr and Cu concentrations in the leaves of the tree species *O. europaea* and *L. japonicum*, with exception for the Cu concentration in leaves taken from the reference sites, there are higher values compared to the given average reference values of Cr and Cu in plants after Markert (1997): up to nine times higher for Cr concentrations and up to four times higher for Cu concentrations. The Pb concentrations detected in all leaves samples reflect a very serious Pb emission problem in and around the region of Baku. Even the lowest Pb concentration measured in the leaves of *P. coccinea* at the reference site (botanical garden) showed a 10 times higher Pb concentration compared to the “normal” average reference concentration of Pb in plants given by Markert (1997). Especially, the more Pb contaminated sample regions site 1 (industry) and site 2 (traffic) showed up to 70 times higher Pb concentrations. The reason for the higher lead values might be the greater use of cars and buses fuelled with leaded gasoline. Industrial and metallurgical processes, as well as the combustion of diesel oil produce the largest emissions of lead. The city’s past as a Soviet industrial center has left it as one of the most polluted cities in the world (Luck 2008). At

site 1, industrial facilities (chemical, pharmaceutical, metallic, petroleum industry) are randomly distributed in the central parts of the region. They represent, together with city traffic and coal power stations, the sources of various types of pollutants (Mitrovic *et al.* 2008; Pavlovic *et al.* 2007). It is known that the main sources of copper and lead pollution are the steel industry and coal combustion (Anagnostatou 2008). These results give an indication that the accumulation of trace metals depend on the traffic, industrial activities, and urbanization levels (Markert *et al.* 2011; Mingorance, Oliva 2006).

Additionally, the results show that the concentrations of all studied elements in *P. coccinea* tissue were comparable to the given “normal” averaged reference ranged values for plants after Markert (1997) with the exception of Pb. These results give the conclusion that the tree species *P. coccinea* is not applicable for bioindication of air pollution. Unlike that situation, the tree species *O. europaea* and *L. japonicum* demonstrate the effects of urbanization on elemental concentrations in leaves, but the results may also depend on the morphological anatomical parameters of leaves (Kardel *et al.* 2010).

Nevertheless, there are some general trends in the data which, notwithstanding effects of selective uptake of metal ions by plants, can be used to show that there are different sources of emission/pollution which contribute to metal contents of the leaves, that is, Pb, and Cr get there from other sources than Fe does (which is quite reasonable), possibly via particles of different sizes and origins or part via soil/ground water, part through atmospheric deposition (total digestion of leaves prior to analysis or complete burning in F-AAS covers both pathways to the leaf). Of course, the three plants differ in both biochemical fractionation behavior (which unfortunately is not yet numerically specified for these three species) when obtaining metal ions from soil and in relative impacts of atmospheric deposition likewise (the leaves are differently thick and “sticky”).

Conclusions

Air pollution with trace metals is a matter of great interest, especially in urban areas (Markert *et al.* 2011). Monitoring of air quality using plants has been widely applied to detect and to monitor the level, distribution and effect of pollution (Gajic *et al.* 2009; Markert *et al.* 2003; Mingorance, Oliva 2006). Although biomonitoring of air quality using plants has been practiced for years in many European countries, it has still not been applied at a satisfactory level, due to different and even opposing results. Trees are very efficient at trapping atmospheric particles, and they play a special role in reducing the level of fine, “high risk” respirable particulates, which have the potential to cause serious

human health problems. The present primary results on trace metal concentrations in leaves of tree species in and around Baku show that especially, the leaves of *O. europaea* and *L. japonicum* can be probably used as bioindicators, because of their ability to accumulate the essential elements Cu, Cr, and Fe. But of highest interest are the Pb concentrations in the environment. Pb is a nonessential element and can lead to toxic effects to humans, animals, and plants alike. So, the present study showed that the leaves especially of *O. europaea* and *L. japonicum* reflect in an excellent way the Pb status of the environment of Baku.

After Sawidis *et al.* (2011) the environmental lead pollution is directly related to the density of traffic. The main part of the total vehicle fleet up to 65% is located in the city of Baku, which significantly affects the ecological background of the city. In addition to the traffic density, industrial activities also tend to increase the concentration. The samples obtained from an industrial area, as well as from urban roadsides, which encounter the highest human activity and vehicular density, had the highest accumulation of the metal concentrations. Most of this contamination can clearly be traced back to motor vehicle traffic emissions.

In general, because the leaves of *O. europaea* and *L. japonicum* as bioindicators are reflecting the environmental status it would be enriching to join global monitoring programs of air pollution.

In conclusion,

- (1) the leaves of *O. europaea* and *L. japonicum* have been used for the first time as possible bioindicators for controlling the air pollution in Baku city; they reflect the environmental status;
- (2) the leaves of *P. coccinea* are not suitable for bioindication.

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