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Arsenic accumulation in some natural and exotic tree and shrub species in Samsun Provience (Turkey)

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Samsun İli'ndeki bazı doğal ve egzotik ağaç ve çalı türlerinde arsenik birikimi

Abstract: The bioaccumulation of metalloids especially arsenic (As) concentrations in urban and suburban environments and bioaccumulation of As in natural and exotic tree and shrub species are not well-documented. One of the most significant sources of As are vehicular emissions and coal combustion. The bioaccumulation of As in some natural and exotic tree and shrub species in Samsun and Atakum in Central Black Sea Region of Turkey is studied. Most of the studies about As pollution were carried out in heavily polluted environments such as lead smelters. However, high As concentrations were found for some natural and exotic tree and shrub species in urban and suburban environments in this study. It has been found that *M. grandiflora* twigs had the highest As concentrations in all of the studied species. Leaf As concentrations were found to be high in *E. camaldulensis*, *P. abies*, *A. cyanophylla*, *C. vitalba*, and *L. vulgare* as compared to twigs and flowers, while twigs of O. *europaea* and *M. grandiflora* had high As concentrations in Samsun center. *E. camaldulensis* and *A. cyanophylla* had high As concentrations in their leaves in Atakum similar to Samsun city center. *M. grandiflora* twigs and L. vulgare leaves can be used for biomonitoring studies due to high As concentrations in their tissues.

Key words: Arsenic, Automobile emissions, Central Black Sea Region, Heavy metal

Özet: Metalloidlerin özellikle arsenik (As) biyoakümülasyonunun kentsel ve kırsal alanlardaki doğal ve egzotik ağaç ve çalı türlerindeki konsantrasyonları pek çalışılmamıştır. Arsenik metaloidinin en önemli kaynaklarından biri taşıt emisyonları ve kömür yanmasıdır. Samsun ilindeki bazı doğal ve egzotik ağaç ve çalı türlerinde arsenik metaloidinin biyolojik birikimi incelenmiştir. Kirlilik gibi çalışmaların çoğu kurşun kirleticileri gibi yoğun kirlenmiş ortamlarda gerçekleştirilmiştir. Ancak, bu çalışmada kentsel ve kırsal ortamlarda bulunan bazı doğal ve egzotik ağaç ve çalı türlerinde yüksek arsenik konsantrasyonları bulunmuştur. İncelenen tüm türlerden, *M. grandiflora* dallarının en yüksek As konsantrasyonnuna sahip olduğu bulunmuştur. *E. camaldulensis, P. abies, A. cyanophylla, C. vitalba* ve *L. vulgare* türlerinde dal ve çiçeklere göre yapraklarda arsenik konsantrasyonu yüksek iken, *O. europaea* ve *M. grandiflora* türlerinde ise dalların yüksek arsenik konsantrasyonlarına sahip olduğu bulunmuştur. Samsun şehir merkezi ve Atakum'da *E. camaldulensis* ve A. *cyanophylla* türlerinin yapraklarında benzer yüksek oranda arsenik konsantarasyonu bulunmuştur. *M. grandiflora* dalları ve *L. vulgare* yapraklarının yüksek arsenik konsantrasyonlarına sahip olmasından dolayı bu türler biyo-izleme çalışmalarında kullanılabileceği belirlenmiştir.

Anahtar Kelimeler: Arsenik, Otomobil emisyonu, Orta Karadeniz Bölümü, Ağır metal

1. Introduction

Due to their immutable nature, heavy metals are a group of pollutants of much concern. Heavy metals and metalloids are known as important environmental pollutants and they are toxic even at very low concentrations. These are usually essential for biological systems, but at high concentrations, they can act in a deleterious manner by blocking essential functional groups, displacing other metal ions, or modifying the active conformation of biological molecules (Alkorta et al., 2004; Korn et al., 2007; Gill et al., 2012).

The presence of metallic and metalloid species in automotive fuels is undesirable and metallic or metalloid elements may derive from the raw product, such as nickel and vanadium in petroleum-based fuel or phosphorus in biodiesel, or they may be introduced during production and storage. In addition to this fuel burning, the wear of auto tires, fluid leakage degradation, and corrosion of metals are the other most important sources of pollution (Sadiq et al., 1989; Wei and Morrison, 1994; Monaci et al., 2000; Suzuki et al., 2009). Motor vehicles have direct and indirect impacts on the metabolism of roadside plants and that automobile emissions caused chronic pollution in the neighboring environment in long term (Ozakı et al., 2004; Akan et al., 2013).

It has been pointed out that Arsenic (As) is an important metalloid although it ranks 20th among the elements in abundance and period 4 of the periodic table (Fishbein, 1981; Wuana and Okieimen, 2011). Koch et al. (2000) found that As is very harmful because large fraction of this metalloid in many plant tissues is not water soluble. These fractions could be bound to lipids or to cell wall components, including in soluble cellulose, calcium or magnesium pectates, or lignin. It has been known that As usually inhibits plant growth because it is affected the uptake of other nutrients and as a result of this metabolic processes such as nutrient transport are altered (Gomes et al., 2012). It is also very harmful for central cellular functions such as aerobic phosphorylation and the function of proteins (Hughes, 2002; Nagajyoti et al., 2010; Bergqvist, 2011). As is toxic for plants, animals, microorganisms, and human beings and sometimes concentration of As in the environment can be reached to toxic levels (Karimi and Souri, 2015).

As pollution in the environment from both anthropogenic and natural sources is a global problem. In many parts of the world As concentrations in the environment have exceeded the safe threshold (Gonzaga et al., 2006). It has been pointed out that automobile emissions exhibit significant increase in the accumulation of As in plants. Coal combustion is also known to be one of the main sources of As in environment. Anthropogenic activities such as mining facilities, urban wastes, sewage sludge, and dye industry are known to be the other main sources of As pollution. (Bajpai et al., 2010).

Biomonitoring has been defined as using of organisms to obtain quantitative information on environmental quality and is a remarkable contribution to traditional monitoring techniques (Gerhardt, 1999). Tree species has long been used for biomonitoring because they are very efficient at trapping atmospheric particles and play a critical role to determine the risk categories for a particular heavy metal and metalloid. They have also been used in phytoremediation and the restoration of mine areas due to their high biomass and productivity (Tomasevic et al., 2011; Favas et al., 2013; Pal et al., 2014).

Traffic intensity has long been known as a great problem for environmental pollution. Because automobile emissions one of the most striking causes of environmental pollution and alarmingly increased from year to year in Black Sea Region (Samsun Security Directorate of Traffc Bureau, 2012). Meharg and Hartley-Whitaker (2002) reported that arsenic accumulation in plant tissues was poorly understood. There were several studies about As concentrations around mine and smelter wastes, in urban environments (Tomaševic et al., 2005; Nkongolo et al., 2008; Xie et al., 2009). However, aquatic species (Koch et al., 2000), lichen species (Bajpai et al., 2010), savanna trees (Gomes et al., 2012), pine species (Favas et al., 2013), and herb species (Karimi and Souri, 2015) were used. However, no study was carried out to evaluate the using of shrub and tree species for biomonitoring of As pollution mainly traffic origin in urban environments. This study is aimed to determine (i) As concentrations in leaf, twigs, and flowers of some natural and exotic tree species in Samsun city (located in Central Black Sea Region of Turkey) and suburb of Samsun (Atakum) mainly originated from traffic density (ii) which plant organ had accumulated the highest As concentration (iii) to compare As concentrations of studied plant species with As concentrations in other plant species (iv) to find which plant species may be used safely for biomonitoring of As pollution.

2. Materials and Method

Sampling

In the present study, 10 exotic and natural tree and shrub taxa (*Laurocerasus officinalis* Roemer (Rosaceae), *Eucalyptus camaldulensis* Dehnhardt (Myrtaceae), *Picea abies* (L.) Karst (Pinaceae), *Acacia cyanophylla* L. (Mimosaceae), *Clematis vitalba* L. (Ranunculaceae), *Olea europaea* L. var. *europaea* (Oleaceae), *Platanus orientalis* L. (Platanaceae), *Ligustrum vulgare* L. (Oleaceae), and *Magnolia grandiflora* L. (Magnoliaceae) were used. Two different regions (Samsun city center and Atakum (suburb of Samsun) which had different traffic densities were selected. Mean traffic density in Samsun city center is 6000 vehicles hr-1, while traffic density is lower in Atakum (the suburb of the city) and mean traffic density is 2000 vehicles hr-1. Leaf, needle and twig samples of studied plant species were used to determine As concentrations.

Five leaves and twigs samples per species, and per plant organ in each region were used. Plant organs were cut off with teflon coated stainless steel scissors using polyethylene gloves. All specimens were taken from the same height and at the same time. Samples were taken from the side facing the highway of the crown. It has been shown that sampling from different sides of the crown did not affect heavy metal concentrations in leaves (Bargagli, 1998).

Taxonomic nomenclature followed that of Guner at al. (2012).

Plant analysis

In the laboratory leaf and twig samples were dried to a constant weight at 60°C with a microwave oven. Dried plant samples were ground by using a hand mortar. Each time, approximately 0.5 g of ground sample was taken and digested using a mixture of HNO_3/H_2O_2 in microwave oven of 360 W for 30 mins. Each digested mixture was diluted to 100 mL volume and centrifuged before the metalloid analysis. A Varian spectra 220/880 flame atomic absorption spectrometer operating with an air/acetylene flame. The spectrophotometer was operated at 193.7 nm with a slit width of 1.0 nm. Air flow was 13.00 L/ /min. Lamp current was 10.0 mA B, and measurement time was 1.0 s. Pre-read delay was 5 s. The carrier gas flow was optimized to 80 mL/min prior to calibration in order to achieve the highest sensitivity (Allen et al., 1986; Allen et al., 1989; Uddin et al., 2013; Engin et al., 2015). The gps coordinates of sampling points were measured by Garmin gps map 60csx device. Sampling points were showed on map according to gps coordinates (Figure 1).

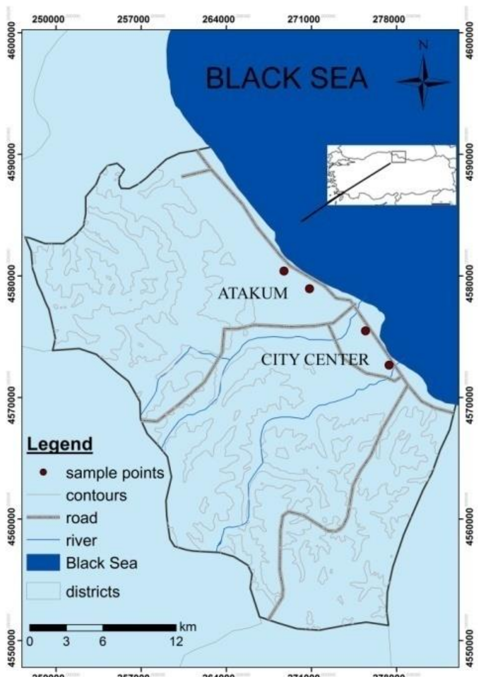

Figure 1. The map of two different regions (Samsun city center and Atakum) which had different traffic densities was selected.

Repeated multivariate analysis of variance (RMANOVA) was used to find the significant differences between studied localities and among plant organs. Tukey's honestly significant difference (HSD) tests were used to rank means by using SPSS 19.0 version. Data was tested for normality using the Kolmogorov-Smirnov test before analysis.

3. Results

It has been found that As concentrations in Samsun city center were two times higher in suburb (Atakum). There were some differences with respect to As concentrations in different plant organs. For example, As concentrations were higher in leaves than twigs in Atakum samples. However, such a pattern was not found in Samsun samples. *M. grandiflora* twigs had the highest As concentrations in all of the studied species.

The highest As concentrations were found in *M. grandiflora* and *L. vulgare*. As concentrations were reached to 3.0 and 2.0 ppm in twigs and leaves of *M. grandiflora* and *L. vulgare*, respectively in Samsun city center (Figure 2).

Leaf As concentrations were found to be high in E. camaldulensis, *P. abies*, *A. cyanophylla*, *C. vitalba*, and *L. vulgare* as compared to twigs and flowers, while twigs of *O. europaea* and *M. grandiflora* had high As concentrations in Samsun city center (Figure 2).

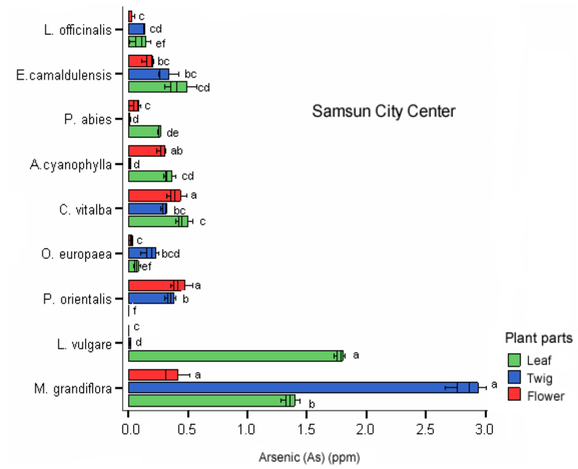

Figure 2. Mean arsenic (As) concentrations and Tukey HSD groups measured at the Samsun city center between plant species of each plant parts. (Different lower case letters indicate significant differences between plant parts. Vertical lines indicate standard error).

Eucalyptus camaldulensis and *A. cyanophylla* had high As concentrations in their leaves in Atakum similar to Samsun city center. However, twigs of *L. officinalis* and *L. vulgare* were higher As concentrations in Atakum (Figure 3).

It has been found that leaf As concentrations in leaf samples which taken from Samsun city center and Atakum were significantly different and leaf As concentrations in Samsun city center were comparatively high. However, As concentrations in twig samples in *L. vulgare* in Atakum were higher than that of twig As concentrations in Samsun city center, while twig As concentrations were found to be high in other plant species which taken from Samsun city center (Figure 4 and Figure 5).

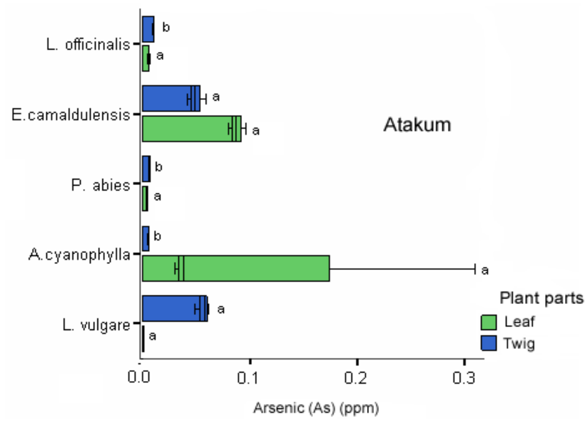

Figure 3. Mean arsenic (As) concentrations and Tukey HSD groups measured at the Atakum city centre between plant species of each plant parts. (Different lowercase letters indicate significant differences between plant parts. Vertical lines indicate standard error).

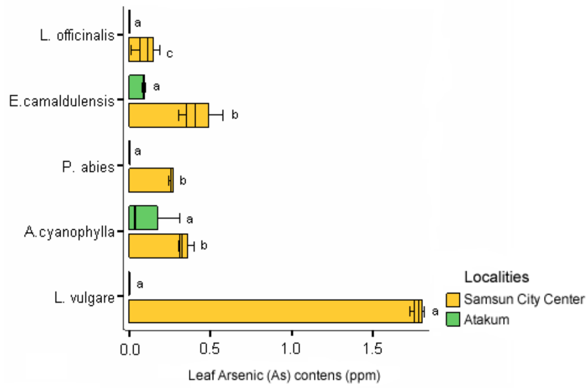

Figure 4. Mean arsenic (As) concentrations and Tukey HSD groups measured at leaves of each plant species between localities. (Different lowercase letters indicate significant differences between plant species. Vertical lines indicate standard error).

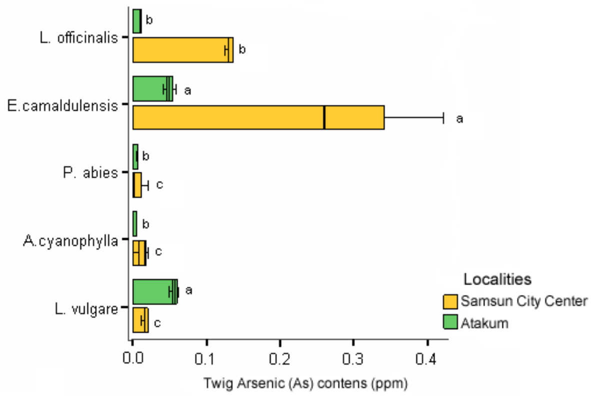

Figure 5. Mean arsenic (As) concentrations and Tukey HSD groups measured at twigs of each plant species between localities. (Different lower case letters indicate significant differences between plant species. Vertical lines indicate standard error).

4. Discussions

As concentrations may be changed regarding traffic density, tree species, and different plant parts. Plants vary in their sensitivity and accumulation of As in their tissues (Meharg and Hartley-Whitaker, 2002) For example, lower As concentrations were found in plant specimens which taken from Atakum where traffic density was comparatively low. This is shown that As accumulation has been changed due to traffic density. High As concentrations were found in the leaves of a coniferous species (*P. abies*) in Samsun city center where traffic density was two times higher than Atakum. In coniferous species, it has been found that leaves had the highest As concentrations and this is evaluated as a plant defense mechanism against As toxicity (Favas et al., 2013). High As concentrations were also found in the leaves of *L. officinalis, E. camaldulensis, A. cyanophylla, C. vitalba* and *L. vulgare* as compared to twigs. Similarly, A. cyanophylla and E. camaldulensis had higher As concentrations in their leaves as compared to twigs in Atakum. These results may be indicated As accumulation in plant species is strongly species-dependent (Bergqvist, 2011).

In plant roots As compounds are sequestered in vacuoles and chelated with thiols and as a result of this the transportation of As compounds are limited (Zhao et al., 2010; Gomes et al., 2012). Zhao et al., (2010) also stated that As has low mobility and translocation from roots to aboveground parts of plants were limited except for hyper accumulator species. On the contrary to such limitations high As concentrations were found in *M. grandiflora* twigs and *L. vulgare* leaves. Because As concentrations in *M. grandiflora* twigs and *L. vulgare* leaves were above the toxicity limit. It has been reported that toxicity limit for arsenic in plants is above approximately 2 mg kg-1 (Kabata-Pendias, 2010; Favas et al., 2013). Low As concentrations were found in several studies although they were carried out in polluted environments as compared to the present study. For example, Nkongolo et al. (2008) found low arsenic concentrations in *Picea mariana* although they studied near smelter sources. Akan et al. (2013) have been reported 0.02-0.21 µg g-1As concentrations in *Azadirachta indica*. Xing et al. (2016) found 0.091 mg/kg As in 25 wheat (*Triticum aestivum*) varieties near the lead smelters in China. As concentrations in some studied species were found to be rather high as compared to similar studies. 3.0 mg kg-1 and1.75 mg kg-1As concentrations were found in *M. grandiflora* twigs and *L. vulgare* leaves, respectively. Dias et al. (2010) also found that As may be translocated to twigs in some plant species. In summary, As is a very important metalloid not only very toxic for plants but also influences the metabolism of the other elements such as N, P, K, Ca and Mg (Tu and Ma, 2005; Gomes et al., 2012). We suggested that As accumulator tree species may been used safely for urban-planning especially in highly-contaminated areas with As. *M. grandiflora* and *L. vulgare* can be used for biomonitoring studies due to high As concentrations in their twigs and leaves, respectively. In general, As concentrations were higher in plant specimens in Samsun city center and population density is higher in Samsun city center than Atakum and automobile emissions and coal combustion are more apparent in Samsun city center. In order to prevent As pollution heavy traffic intensity should be restricted. For example, odd- and even-numbered vehicles plates may be exit to traffic on alternating days. In addition to this, coal combustion should be prohibited and the usage of renewable resources such as natural gas should be put into practice.

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