Ficus retusa L. as possible indicator of air metallic pollution in urban environment
Sahli Leila, Belhiouani Hadjer

Leila Sahli (sahli.leila@umc.edu.dz)
Université Constantine 1: Universite Constantine 1 https://orcid.org/0000-0002-3722-349X
Hadjer Belhiouani
Université Constantine 1: Universite Constantine 1

Research Article

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Abstract

The tree species differed by their capacity to capture air-borne dust and to allocate trace element from contaminated soil. The aim of this study was to explore the accumulation potential of heavy metals (HMs) by *F. retusa* L. and its possible use for air pollution biomonitoring in urban areas. Plant material was sampled along the national roads in Constantine city (NE-Algeria), characterized by an intense traffic load. The concentrations of cadmium, copper, lead and zinc were determined in the washed and unwashed leaves. The mean concentrations of HMs decrease in the following order: Zn > Pb > Cu > Cd for both studied leaves, and were about 0.68 and 0.98 µg/g for Cd, 7.26 and 8.74 µg/g for Cu, 20.35 and 37.61 µg/g for Pb and 63.33 µg/g and 75.94 µg/g for Zn, for washed/unwashed leaves respectively. The studied metal contents were significantly higher than those cited in the literature; this indicates the traffic road impact on HMs emissions and uptake by plants. Higher values of metal accumulation index (MAI) indicate the effectiveness of the studied species for monitoring air metallic pollution in urban areas, and its usefulness for phytoextraction of HMs from the polluted soils and/or air. Results of this study could be beneficial as preliminary reference values for HMs uptake by *F. retusa* in urban environments.

1. Introduction

With the continuous improvement and development in our quality of life, urban air quality has become a clearly growing problem and an important area of concern for the scientists. As a result of this development, a various kinds of pollution have been produced. Among the various pollution problems, air pollution has caused major concern over the world due to its widespread nature, damage to our environment anfd potential health risk to humans. This kind of pollution constitutes clearly a growing problem in urban environments (Chen et al. 2016; Zhao et al. 2016; Hao and Wang, 2012; Sawidis et al. 2011), and is currently one of the foremost environmental health problems (von Schneidemesser et al. 2019). Understanding urban air pollution is fundamental to city government and planning. Monitoring helps in assessing the level of pollution in relation to the ambient air quality standards. However, traditional monitoring of pollutants in the air does not provide relevant information on the effects that they could have on living organisms; biological monitoring of air quality is thus more effective (Allajbeu et al. 2017; Simon et al. 2014; Balasooriya et al. 2009). On the other hand, the most important question does not concern the absolute concentrations of a pollutant in the environment, but rather, the reaction of ecosystems and species to the pollutant (Balodis et al. 1993). Indeed, there is no better indicator of the status of a species or a system than the species or the system itself (Tingey 1989).

Of the numerous air pollutants, HMs have received great attention because of their non-biodegradable, and persistent nature, as well as toxic and disruptive effects on living organisms even at low concentrations (Gholizadeh et al. 2019; Gautam et al. 2016). Over the past decencies, the use of plants for HMs pollution monitoring has drawn considerable attention of scientists' worldwide (Safari et al. 2018; Birke et al. 2018; Mukherjee et al. 2016; Serbula et al. 2013; Fowler et al. 2009; Malandrino et al. 2006; Gerdoll et al. 2000; Tyler 1990). The use of plants as a passive sampler in biomonitoring has the advantage of high spatial and temporal distribution and a low sampling cost (Sawidis et al. 2011). Due to their exclusive dependence on the air, lichens and mosses are considered to be the best bioindicators; they are in the forefront of researches (Berdonces et al. 2017). However, in highly contaminated environments, particularly in urban areas where anthropogenic pressure is high, we often see the scarcity or even the total disappearance of these organisms. Thus, higher plants that persist can be used for air quality biomonitoring (Safari et al. 2018; Allahabadi et al. 2017; Mukherjee et al. 2016; Al-Khashman et al. 2011; Gratani et al. 2008; Berlizov et al. 2007; Malandrino et al. 2006; Tomasevic et al. 2005; Dongarra et al. 2003; Pacheco et al. 2002). In urban areas, trees acts as a real pollutant sink. Nowadays, they are the most commonly used as bioindicators in air quality biomonitoring studies, as they do not change their position within the landscape, some species are evergreen, and subject to pollutants permanently, they are long-lived organisms that can reflect the effects of chronic exposure to metals, offer a great availability of the biological material, and are usually easier to identify as compared to other organisms such as fungi, algae, lichens, or mosses (Allahabadi et al. 2017; Berdonces et al. 2017; Kandziora-Ciupa et al. 2016; Geras'kin et al. 2011; Balasooriya et al. 2009; Berlizov et al. 2007).

In the eastern Algeria, especially in Constantine city, for several years there has been a progressive problem of pollution linked to important road networks, but also to industrial and agricultural activities. Thus, over the last decade, a lot of attention has been paid to terrestrial and aquatic ecosystems in this city; considered environmentally loaded and unhealthy. Indeed, high levels of HMs were found not only in soil, water and sediment (Sahli et al. 2020; El Hadef El Okki et al. 2015; Sahli et al. 2011), but also several studies detected extremely high levels of HMs in herbaceous plants (Zekri et al. 2019). HMs accumulation in the plant largely depend on plant organ (leaf, bark, etc.) and species characteristics including growth rate and biomass (Birke et al. 2018). The leaves of trees have been widely used as indicators of air metallic pollution than other parts of the tree like barks, buds, flowers, and needle, due to their ability to absorb pollutants through stomata and cuticles. They intercept pollutants from atmospheric deposition, both wet and dry, but also accumulate those from the soil (Safari et al. 2018; Allahabadi et al. 2017; Mukherjee et al. 2016; Baldantoni et al. 2014). Numerous researchers, for example, have used *Nerium Oleander* L. leaves (Santos et al. 2019; Fernandez Espinosa and Rossini 2006), *Robinia pseudoacacia* leaves (Alahabadi et al. 2017; Cicek and Koparal, 2004), Pine needles (Turkyilmaz et al. 2018; Pająk et al. 2017), etc. In Algeria, studies were carried out on HMs accumulation by *Platanus acerifolia*.Wil and *Cupressus sempervirens* L. (Maatoug et al. (2007), *Casuarina equisitifolia* L. (Lakhdari and Benabdeli, 2012), *Tamarix gallica* (Krika et al. 2013), *Eucalyptus cladocalyx* and *Cupressus. sempervirens* (Alatou and Sahli 2019). To our knowledge, there are few studies on the use of the genus Ficus for air quality monitoring. Indeed, the determination of heavy metal contents has been focused on leaves of *Ficus Benjamin* (Guzman-Morales et al. 2011) and *Ficus microcarpa* (Rossini and Rautio 2005) in urban areas.

F. retusa is a tropical evergreen tree of the family Moraceae, highly valued for its resistance, and its emission of aerial roots, which give it a lot of character. Its small size and large trunk make it a very decorative plant, ideal for contemporary decorations. *F. retusa* was introduced in Constantine city (NE-Algeria) during the year 2014–2015 as a part of the event "Constantine, as capital of Arab culture 2015". Thus, in and around Constantine city, *F. retusa* was planted along roadsides for beautification. Regarding the fact that this species has been introduced in several cities in Northern Algeria, which are known as mostly polluted, we want through this investigation, to explore the potential of *F. retusa* to accumulate and tolerate HMs in its tissues. Thus, cadmium, copper, lead and zinc concentrations were assessed in washed and unwashed leaves of *F. retusa* collected in a contaminated area (Constantine, Algeria), in order to highlight the usefulness of using this species as a bioindicator of air metallic pollution.

2. Material And Methods

2.1. Study area and sampling sites

This study was conducted in Constantine, a city in the Northeast of Algeria, located at a longitude of 6°36'52" Est, a latitude 36°21'54" Nord, and an elevation of about 574 m above mean sea level, at 245 km of the Algerian-Tunisian borders, 431 km of the capital Algiers to the west, 89 km of Skikda to the north and 235 km of Biskra to the south. This city with an area of 2197 km² has high population density estimated at 750000 inhabitants. It is characterized by a semi-arid climate, with rainfalls ranging from 350 to 650 mm, and an average temperature ranging from 25 to 40°C in summer and 0 to 12°C in winter. In this region, the winds blow in a dominant direction North-West and North with air masses coming from the mountains. Also, this region is characterized by southerly winds, which blows particularly in mid-summer to late fall. There are many industrial activities around this city (e.g. steel, ceramic tile, *industrial gases industry, tobacco and tobacco-related products,* and pipe industries). The most important are located within a radius of 20 km around Constantine City (Sahli et al. 2011). The car fleet in Constantine city shows typical mixing of different transport mode in the road network of the country when a national road passes urban center (tourism vehicle, truck, coach, motorcycle, road tractor, etc.). The volume of vehicles in Constantine city is very high. Given its geographical location, Constantine city is a major corridor that serves over 231.521 vehicles per day, and traffic congestion in this area is very heavy. Congestion is experienced while the national road is passes the city center, but also near economic zones and industrial parks. Older vehicles predominant in Vehicle Park, the new cars represent only 5.58%. An *old* car is far more *polluting* than a modern *vehicle.* Samples were collected from twenty sampling sites selected in the city center, along the national roads connecting Constantine city to the capital Algiers and other cities, characterized by an intense traffic load. Sampling locations within the region are depicted Figure 1.

2.2. Sample collection and preparation

The determination of heavy metal contents was conducted on the leaves of *F. retusa* taken from the selected sites during February/March 2020. Leaves were taken randomly at each sampling site from three adult *F. retusa* trees which were of about the same age in order to have the same integration time of metal pollution. For this, each tree species with similar height and trunk diameter were selected. All selected trees had around five to six years old at the time of sampling. In general, the trunk diameter and height of *F. retusa* were 19.5 to 30 cm and 3 to 3.5 m. For sampling, leaves with identical length, fully expanded, and with no spots, and abnormal or imperfection appearance (chlorosis, necrosis, insect infestation) were considered as sample. Trees with unusual leaf such as wrinkled or yellow leaf must be excluded (Safari et al. 2018). Leaves sub-samples were bulked to obtain a representative sample for each investigated site. Plant material was taken from different quarters of canopy (in the upper, middle and lower crown of each tree). A sub-sample was washed with tap water followed by deionized water to remove any dust deposits and particulate matter, whereas the other one remained unwashed to the sake of evaluating the real shape of atmospheric pollution. Then, all samples were dried at 85°C and ground.

2.3. Analysis of heavy metals in leaf samples

Mineralization of the samples and HMs extraction in plant tissue was carried out according to the method described by Benton (2001). It consists of a dry ashing of the ground samples (1 g of each representative sample) in a muffle furnace hang 4 to 8 h with a gradual rise of temperature reaching 500°C. After cooling, 10 ml of diluted aqua regia (1/3) was added to dissolve the ash. To assist the ash solubilization, crucible contents was heated. The obtained solutions were filtered using a Whatman filter paper (Whatman 540), diluted to a volume of 20 mL with deionized water, and stored in polyethylene bottles at 4°C until analysis. The concentrations of Cd, Cu, Pb, and Zn were measured by atomic absorption spectrophotometer (Shimadzu AA-6800).

The accuracy of the analytical method used for HMs was checked by analysis of blank samples and standard reference materials (Certified reference Material BCR62 *Olea europea* Leaves). The percentages of recovery of both reference materials for Cd, Cu, Pb, and Zn were better than 91%.

2.4. Data analysis

Statistical analyses were conducted using Statistica 7.0 software. First, descriptive statistics including mean, median, standard deviation, minimum, and maximum were determined. Furthermore, an independent-samples t-test was conducted to compare results of washed leaves to unwashed one. The level of significance was set at p value (of 5%).

Different tree species have different ability to accumulate atmospheric HMs. Therefore, we used MAI to assess the overall performance and ability of *F. retusa* for HMs accumulation. MAI was calculated as follows:

$$\boldsymbol{MAI} = \frac{1}{n}\sum_{i=1}^{n} Ij$$

Where n is the total number of HMs, and Ij is the sub-index for variable j, obtained by dividing the mean concentration (x) of each HMs by its standard deviation (Liu et al. 2007; Hu et al. 2014; Khalid et al. 2019).

3. Results And Discussion

3.1. Plant parts HMs contents

Statistical results of heavy metal contents for washed leaves (WL) and unwashed leaves (UL) of *F. retusa* are summarized in Table 1. Extreme values, mean, median and standard deviation of cadmium, copper, lead and zinc contents were given. Clearly, the mean concentrations of HMs decrease in the following order: Zn > Pb > Cu > Cd for washed and unwashed leaves.

Results showed that HMs quantified in washed and unwashed leaves vary from one site to another whatever the metal. Thus, for cadmium, concentrations ranged from 0.25 to 0.89 µg/g, and from 0.68 to 1.2 µg/g with mean values of about 0.68 and 0.98 µg/g for washed and unwashed leaves, respectively. The natural concentration of cadmium in plant tissues ranges from 0.1 to 2.4 µg/g (Nagajyoti et al. 2010). Comparison of our results with these findings showed that Cd accumulation for all samples never exceed the extreme value of this range. Besides, concentrations were below the phytotoxic range specific to leaves (5–10 µg/g), reported by Alloway (2013). Comparing our results with exiting literature showed that they largely exceed those reported by Fazrul and Huda (2018) for the leaves of *Athyrium esculentum* (0.01 µg/g), *Chromolaena odorata* (0.01 µg/g), and *Lantana camara* (0.09 µg/g) harvested from a roadside in the Jengka sub-urban area in Pahang, Malaysia. Likewise, concentrations recorded for *F. retusa* were two to three times greater than those reported by Alahabadi et al. (2017) for unwashed leaves of *Robinia pseudoacacia* (0.5 ± 0.21 µg/g), *Pinus eldarica* (0.62 ± 0.09 µg/g), *Olea europaea* (0.45 ± 0.17 µg/g), and *Cupressus arizonica* (0.38 ± 0.22 µg/g) sampled in the urban area of Yazd in Iran. Results were also higher than those reported by Alfani et al. (2000) for leaves of *Quercus ilex* collected in the urban area of Naples. Authors recorded the following concentrations: 0.01 to 0.09 µg/g for the urban and suburban parks, 0.07 to 0.21 µg/g for urban roads with different traffic flows, and 0.007 to 0.01 µg/g for the control site. However, results were comparable to those of Abou El Saadat et al. (2011) recorded for leaves of the same species sampled in a sub-urban (0.38 µg/g), urban (0.90 µg/g) and industrial areas (1.11 µg/g). And those reported by Cicek and Koparal (2004), for leaves of *Salix alba* L., *Populus tremula* L., *Robinia pseudoacacia* L., *Quercus infectoria* L., *Pinus nigra* Arn. ssp. *pallasiana* (Lamb) Holmboe, taken at various distances from the Tuncbilek Thermal Power Plant (Kütahya Province, Turkey). Concentrations recorded ranged between 0.1 to 2.73 µg/g. Cadmium is regarded as one of the most toxic trace elements in the environment and is particularly hazardous because of its easy uptake by plants (Das et al. 1997). It is a non-essential element that negatively affects plant growth and development. Yet, its properties close to those of calcium, allowing it to cross biological barriers and accumulate in tissues. When present in the atmosphere, it may be absorbed via plants' foliar organs after dry and/or wet deposition of atmospheric fallouts on plant canopy (Shahid et al. 2016). Most of the Cd taken by the plant is stored in the cuticle and cell walls in insoluble form and does not migrate into the plant (Tremel-Schaub and Feix 2005). In urban area, cadmium is released into the environment by Vehicle tires, combustion of fossil fuel, municipal solid waste incineration, and the combustion of vehicle lubricating oils (Hu et al. 2014). It is widely used in the production of nickel-cadmium batteries, corrosion control, electroplating, pigments and as a plastic stabilizer (Markert 1992).

Copper concentrations ranged from 5.56 to 9.02 µg/g, and from 6.11 to 11.2 µg/g with mean values of about 7.26 and 8.74 µg/g for washed and unwashed leaves, respectively. According to Alloway (2013), the normal range of Cu concentrations in the plants is 4–15 µg/g, and its phytotoxic concentrations range for leaves tissue is 5–40 µg/g. In the present study, measured concentrations for both studied leaves never exceeded the extreme values range of the normal and phytotoxic concentrations. Concentrations recorded were also below the normal (3 to 30 µg/g) and phytotoxic ranges (20 to 100 µg/g) suggested by Kabata and Pendias (2001) for land pants. Otherwise, concentrations recorded in this study were in the range of concentrations (2.1 to 59 µg/g) recorded by Cicek and Koparal (2004), for leaves of *Salix alba* L., *Populus tremula* L., *Robinia pseudoacacia* L., *Quercus infectoria* L., *Pinus nigra* Arn. ssp. *pallasiana* (Lamb) Holmboe, sampled at various distances from the Tuncbilek Thermal Power Plant (Kütahya Province, Turkey). They were lower than those recorded by Alaimo and Varrica (2020) for unwashed leaves of *Ficus macrophylla* collected in the city of Palermo (Italy); concentrations ranged between 16 and 99 µg/g, and than those reported by Fazrul and Huda (2018) for the leaves of *Athyrium esculentum* (18.5 ± 1.83 µg/g), *Chromolaena odorata* (23.35 ± 2.89 µg/g), and *Lantana camara* (26.85 ± 0.77 µg/g) taken from a roadside in the Jengka sub-urban area in Pahang, Malaysia. Nevertheless, concentrations recorded for washed and unwashed leaves of *F. retusa* were largely higher than those reported by Alahabadi et al. (2017) for unwashed leaves of *Robinia pseudoacacia* (4.45 ± 1.83 µg/g), *Pinus eldarica* (3.08 ± 1.35 µg/g), *Olea europaea* (3.56 ± 1.68 µg/g), and *Cupressus arizonica* (3.23 ± 1.23 µg/g) sampled in the urban area of Yazd in Iran. And also higher than those reported by Alfani et al. (2000) for leaves of *Quercus ilex* collected in the urban and suburban parks of Naples (0.64 to 2.42 µg/g), but lower than those recorded for urban roads with different traffic flows (4.05 to 87.24 µg/g). Among HMs, Cu is an essential element that is required in very small amounts for optimum plant growth and development (Alloway 2013). Most of the plant species can accumulate substantial quantities of copper under natural and anthropogenic condition (Serbula et al. 2012). At low amount, Cu helps in enhancing the plant photosynthesis (Gad 2012). It involves in physiological functions and is a crucial cofactor for many metaloprotiens (Yruela 2005), and plays an imperative function in CO_2 assimilation and ATP synthesis (Pichhode and Nikhil 2015). Moreover, at optimum level, copper is a valuable element of various enzymes involved in oxidation-reduction reactions (Celik et al. 2005). Nevertheless, Cu when present in soil in high amount becomes highly toxic for plants. It can cause cytotoxic injury to plants, this can hinder plant growth and cause chlorosis (Lewis et al. 2001). Copper can be released into the urban environment as a result of wear of the automobile oil pump (Lu et al. 2010). Cu contamination can also be attributed to brake wear from vehicles (Yesilonis et al. 2008), and used in automotive radiators considering its high corrosion and strength (Chen et al. 2014).

For lead, concentrations ranged between 16.12 and 24.86 µg/g with a mean value of about 20.35 µg/g for washed leaves, and from 31.92 to 43.1 µg/g with mean value of about 37.61 µg/g for unwashed ones. According to Kabata-Pendias and Pendias (2001) and Vamerali et al. (2010), the normal Pb concentration in plant tissue can be in the range of 0.1–10 µg/g, and its toxic level is from 10 to 20 µg/g, respectively. In the present study, mean concentrations largely exceed the normal and phytotoxic concentrations. Compared to literature, our results were extremely higher than those recorded by Alaimo and Varrica (2020) for unwashed leaves of *Ficus macrophylla* collected in the urban area of Palermo (Italy); concentrations ranged between 0.49 and 8 µg/g, and those of Fazrul and Huda (2018) for leaves of *Athyrium esculentum* (0.35 ± 0.02 µg/g), *Chromolaena odorata* (0.41 ± 0.01 µg/g), and *Lantana camara* (0.80 ± 0.03 µg/g) sampled in sub-urban area in Pahang, Malaysia. Concentrations were also greater than those reported by Alahabadi et al. (2017) for unwashed leaves of *Robinia pseudoacacia* (0.71 ± 0.21 µg/g), *Pinus eldarica* (3.71 ± 1.81 µg/g), *Olea europaea* (1.27 ± 0.15 µg/g), and *Cupressus arizonica* (0.75 ± 0.10 µg/g) sampled in the urban area of Yazd in Iran. They were also too high compared to those recorded by Singh Patel et al. (2015) for the leaves of *Ficus religiosa* (1.8 µg/g) collected in an industrial area near the city of Korba in India, than those of Abou El Saadat et al. (2011) recorded for leaves of *F. retusa* sampled in a sub-urban (1 µg/g), urban (5.02 µg/g) and industrial areas (18.64 µg/g), in Northern Egypt, and those reported by Alfani et al. (2000) for leaves of *Quercus ilex* collected in the urban area of Naples. The latter recorded the following concentrations: 1.30-20.36 µg/g for the urban and suburban parks, and 0.1 to 0.5 µg/g for the control site. However, concentrations were in the range of those recorded by the same author for urban roads with different traffic flows (3.66–148 µg/g), and those recorded by Matin et al. (2016) when monitoring Cd, Pb, Ar, and Hg in honey bees, propolis, and pine tree leaves in an industrial areas in Izmir, Turkey; concentration were in the range of 35 to 52 µg/g. Although lead is not an essential element for plants, it gets easily absorbed and accumulated in different plant parts. Deng et al. (2016), through their study concluded that the atmospheric deposition is the major cause of Pb, Cd, Cu, Cr, and Zn accumulation in plants of peri-urban and smelting contaminated sites in Baoji, China. Indeed, plants can readily uptake Pb from atmosphere after deposition on their leaves (Turer et al. 2001; Hu et al. 2014). Vehicle emissions are considered as one of the main sources of heavy metal contamination in urban environments (Duong and Lee 2011). The relationship between traffic intensity and the level of Pb has been reported previously in the literature (Chung and Li 2001; Yilmaz and Zengin 2004). HMs produced by vehicular exhaust and road, tire and brake abrasion can be deposited as road dust by dry and/or wet atmospheric deposition (Duong and Lee 2011; Thorpe and Harrison 2008). Constantine city and especially the urban area have a high traffic flow density, constituted by a fleet of vintage cars. In Algeria, lead tetraethyl-containing gasoline is still widely used; almost 90% of old cars still use leaded gasoline. Leaded gasoline contains tetra ethyl lead as an anti-knocking agent, which produces major amounts of lead oxide in automobile exhaust along with traces of tetra ethyl lead. It is also used for the engines valves lubricating. Indeed, Sellami et al. (2020) when using the X-ray fluorescence analysis of marketed gasoline showed that it contains 0.982 g/L of lead corresponding to 1.53 g of tetraethyl lead per liter of gasoline. In addition, Oucher et al. (2015) when studying the magnitude of air pollution by HMs associated with aerosols particles in Algiers recorded a concentration of about 299.3 ng/m^3 and concluded lead comes naturally from the use of the leaded gasoline.

Zinc concentrations ranged between 47.56 and 77.45 µg/g with a mean value of 63.33 µg/g for washed leaves, and between 63.89 and 82.34 µg/g with mean values of about 75.94 µg/g for unwashed ones. According to Alloway (2013), the normal concentrations of Cu in plant tissue is about 60 µg/g, and its phytotoxic concentrations range for leaves tissue is 100–500 µg/g. In the present study, mean values for both studied leaves were 1.06 to 1.37 times higher than the normal concentration, but below the toxic level. Moreover, concentrations were in the range of the normal ones (10–150 µg/g) reported by Markert (1992), Padmavathiamma and Li (2007), and Hu et al. (2004). They were below the critical toxic level fixed at (100 µg/g) by Allen et al. (1974), and Yilmaz and Zengin (2004). Comparison of zinc concentrations in the study area and those recorded in cities around the world, showed that our results were extremely higher than those recorded by Alaimo and Varrica (2020) for unwashed leaves of *F. macrophylla* collected in the urban area of Palermo (Italy); concentrations ranged from 14.5 to 31 µg/g, and those reported by Alahabadi et al. (2017) for unwashed leaves of *Robinia pseudoacacia* (27.2 ± 14.29 µg/g), *Pinus eldarica* (33.25 ± 7.45 µg/g), *Olea europaea* (27.23 ± 14.42 µg/g), and *Cupressus arizonica* (26.1 ± 6.08 µg/g) sampled in the urban area of Yazd in Iran. They were in the range of those recorded by Abou El Saadat et al. (2011) for leaves of *F. retusa* sampled in a sub-urban (40.03 µg/g), urban (67.39 µg/g) and industrial areas (76.31 µg/g). in Northern Egypt, and lower than those recorded by Serbula et al. (2012) for leaves of *Robinia pseudoacacia* sampled in an urban-industrial zone in the municipality of Bor in the Eastern part of Serbia. Concentrations ranged from 49.6 to 100.3 µg/g, and 118.4 to 192.7 µg/g for washed and unwashed leaves, respectively. Zinc is an essential element for all organisms; it is required for various physiological functions of plants at low levels (e.g., 20–100 µg/g dry weight in leaves). Zn is a building block for enzymes, as it activates many enzymatic reactions (Mousavi 2013; Serbula et al. 2012). It is also useful for the maintenance of biomembrane integrity and protein synthesis (Cakmak 2000). However, at high concentrations (e.g., above 200 µg/g d.w. in leaves), Zn has toxic effects on plants (Adriano, 2001). It can impair root development, alter xylem anatomy, modify biomass accumulation patterns, and reduce photosynthesis (Fuentes et al. 2007). Zn excess in urban area is mainly due to vehicular traffic, wearing of brake linings and road surfaces, losses of oil and cooling liquids, corrosion of galvanized automobile parts, and nonferrous plant emissions (Vanni et al. 2015). Zn, added to tires during the vulcanizing process, comprises 0.4 to 4.3% of the resulting tire treads (Chen et al. 2012).

Table 1

Descriptive statistics of heavy metal concentrations (µg.g) in washed (WL) and unwashed leaves (UL) of *F. retusa* from the study area.

Sites	**Cd**		**Cu**		**Pb**		**Zn**	
	WL	**UL**	**WL**	**UL**	**WL**	**UL**	**WL**	**UL**
1	0.82	1.06	8.73	9.52	22.24	41.92	66,31	78,61
2	0.71	1.00	5.78	7.25	19.02	33.76	68,32	79,19
3	0.62	0.92	6.32	7.44	19.50	33.84	57,65	64,82
4	0.74	1.02	8.89	10.02	21.98	41.44	72,81	81,22
5	0.54	0.88	6.02	7.32	21.42	37.46	67,23	78,53
6	0.64	0.96	5.98	8.03	20.18	34.48	65,41	81,62
7	0.58	0.94	6.44	7.96	18.64	33.58	64,52	79,31
8	0.62	1.00	8.56	11.2	21.90	40.22	68,23	77,62
9	0.25	0.68	7.14	9.23	17.62	31.92	59,11	78,21
10	0.88	1.16	8.01	9.98	22.18	41.82	71,87	82,34
11	0.78	1.08	5.78	6.11	21.08	35.64	55,36	75,11
12	0.72	1.04	6.79	8.23	21.68	38.88	77,45	80,02
13	0.86	1.10	8.78	10.3	22.44	42.02	60,23	70,81
14	0.83	1.20	9.02	9.68	20.25	43.10	47,56	68,46
15	0.77	0.85	5.56	6.58	17.56	36.50	69,35	78,69
16	0.53	0.79	6.35	7.89	19.23	33.26	51,25	63,89
17	0.65	0.93	7.02	8.89	18.96	34.05	56,89	69,77
18	0.71	0.98	8.23	9.97	20.23	37.18	63,25	78,92
19	0.83	1.02	7.89	9.02	24.86	41.20	61,28	75,41
20	0.89	1.13	8.06	10.25	16.12	40.10	62,71	76,33

[a]Nagajyoti et al. (2010)
[b]Alloway (2013)
[c]Kabata-Pendias and Pendias (2001)
[d]Vamerali et al. (2010)

Sites	Cd		Cu		Pb		Zn	
	WL	UL	WL	UL	WL	UL	WL	UL
Min	0.25	0.68	5.56	6.11	16.12	31.92	47,56	63,89
Max	0.89	1.2	9.02	11.2	24.86	43.1	77,45	82,34
Mean	0.69	0.98	7.26	8.74	20.35	37.61	63,33	75,94
Median	0.71	1.00	7.08	8.95	20.24	37.32	63,88	78,37
SD	0.15	0.13	1.20	1.39	2.08	3.65	7,40	5,47
CV(%)	21.43	12.60	17.02	15.56	10.26	9.77	11,59	6,98
Normal range in plant Tissue	0.1-2.4[a]		4-15[b]		0.1-10[c]		60[b]	
Phytotoxic concentration in plant tissue (leaves)	5-10[b]		5-40[b]		10-20[d]		100-500[b]	
[a]Nagajyoti et al. (2010)								
[b]Alloway (2013)								
[c]Kabata-Pendias and Pendias (2001)								
[d]Vamerali et al. (2010)								

Furthermore, the levels of trace metals in washed leaves samples were lower than those in unwashed ones. Student's t-test showed that there is a significant difference between contents of Cd, Cu, Pb and Zn at ($p < 0.001$) in washed and unwashed leaves. As shown in Table 2, the amount of metals in the investigated area removed from the leaves by washing differed greatly from one metal to another. This removal process depends on the contaminant level in the sample. Thus, 9.41 to 63.24 % of cadmium, 5.40 to 25.53 % of copper, 39.66 to 59.80 % of lead, and 3.21 to 30.53 % of zinc were removed by the washing process. The removal of a high percentage of HMs from the plant leaves by washing suggests the areal deposition of air-born particles; the contamination of plants occurs mainly by retention of particulate matter. Amount of accumulated metals might be related to road distance and traffic volume, and can be removed through washing as reported by Swaileh et al. (2004). Foliar analysis is particularly helpful to detect elements present in the air in tiny concentrations or only temporarily. The concentration of essential and non-essential elements in leaves may provide information on the incidence of each element in the environment (Alfani et al. 2000). Analysis of unwashed leaves is, therefore, to be considered as a good method to assess the degree of air contamination because it provides an evaluation of elemental content of leaf surface deposit whilst analyses of washed leaves emphasis the fraction of elemental content taken up by roots. Nevertheless, absorption of trace elements from the soil *via* the root system cannot be ruled out, though there is evidence, at least for Pb, that translocation from the roots to the shoot of the plant is not the main pathway (Hu et al. 2014; Turer et al. 2001; Kabata Pendias and Pendias 1984).

Table 2
Percentages of Cd, Cu, Pb and Zn removed by washing procedure from leaf samples of *F. retusa*.

Statistics	Cd	Cu	Pb	Zn
Min	9.41	5.40	39.66	3.21
Max	63.24	25.53	59.80	30.53
Mean	29.92	16.76	45.71	16.72
SD	10.62	5.57	4.68	6.15

3.2. Assessment of HMs accumulation capacities using metal accumulation index (MAI)

As mentioned before, we used metal accumulation index to assess the overall performance of *F. retusa* in terms of metal accumulation. Results of Cd, Cu, Pb, and Zn mean metal accumulation sub-index and MAI for washed and unwashed leaves of *F. retusa* are shown in Fig. 2. The sub-index metal accumulation values for the washed and unwashed leaves of *F. retusa* within the studied sites were about 4.55 and 7.83 for Cd, 6.03 and 6.27 for Cu, 9.80 and 10.32 for Pb, 8.55 and 13.88 for Zn. The MAI values were about 7.23 and 9.57 for washed and unwashed leaves, respectively. Tree leaves in urban area are exposed to the air and the soil splash. Roadside heavy metal concentration, and consequently the differences in sub-index and MAI values largely depend on the local atmospheric chemistry and changes, meteorology properties, and plant characteristics (Yin et al. 2011; Hofman et al. 2013, Hu et al. 2014). Furthermore, other factors, such as highway characteristics (tunnel, structure, and gradient), roadside terrain and distance, traffic conditions (traffic volume, fleet speed, vehicle type, and age), vehicle performance (engine, fuel, and accumulating mileage), driving behavior (acceleration and deceleration), as well as sampling sites and altitude, result in dramatic changes in HMs air emission, and therefore, affect the ability to remove air pollutants by urban vegetation. The percentage of oxygen in the atmosphere decreasing with the increment of altitude can influence the efficiency of gas consumption and vehicular emission mechanism. Previous research focusing on the effect of altitude on vehicle on-road emissions indicated that vehicular emissions at high altitude can be much higher than observed at sea level (Bishop et al. 2001; Chaffin and Ullman 1994).

Compared to literature, the obtained MAI values were lower than those recorded by Nadgórska-Socha et al. (2017). The mean metal accumulation indexes were about 17.51 for *Betula pendula*, and 10.83 for *Robinia pseudoacacia* sampled in Dabrowa Gornicza city in the southern part of Poland (Slaskie province, a known industrialized region of the country). Metals taken into consideration in this study were Cd, Cu, Fe, Mn and Zn. However, our results were higher than those obtained by Monfared et al. (2013) for

Robinia. pseudoacacia (2.21), *Fraxinus rotundifolia* (1.9), and *Platanus orientalis* (2.09). Those authors took into consideration Cd and Pb levels in plants leaves sampled in Karaj the center of the Alborz province in Iran. They were higher than those obtained by Roy et al. (2020) in an industrial site (Jamshedpur in Jharkhand, India) for *Ficus bengalensis* (5.15 mg/kg), *Ficus Religiosa* (3.92), *Saraca aoca* (3.77), *Azadirachta indica* (3.27), *Mangifera indica* (2.55), *Psidium guajva* (2.30), *Alstonia scholaris* (2.23), and *Ailanthus excels* (2.13). They were also higher or close to those recorded by Karmakar and Padhy (2019) for *Shorea robusta*, *Acacia auriculiformis*, *Eucalyptus globulus* and *Azadirachta indica* sampled in the Barjora forest (West Bengal, India) situated adjacent to heavy pollution sources. The metal accumulation index ranged between 9.48 and 9.82, 4.29 and 6.08, 5.04 and 11.65, 5.21 and 7.98 for the studied species, respectively. According to Liu et al. (2007) plants with a high value of MAI would be a good choice for planting in areas where HMs pollution is a problem. These plants should be used as natural barriers against pollution, especially for vulnerable areas, like parks, schools and residential areas (Zhai et al. 2016; Hu et al. 2014). *F. retusa* seems have a remarkable ability for HMs accumulation and to be a good phytoextractor, so it would be interesting, to select it for air quality monitoring and for urban greening. Therefore, its role in biomonitoring will be of great importance especially in urban areas, where other groups of plants are lacking. Results of this study highlighted and confirm the usefulness of trees especially *F. retusa* in the monitoring and the identification of different metal sources.

4. Conclusion

The aim of this study was to assess and explore the potential of *F. retusa* for HMs accumulation and air quality monitoring. Its ability to act as bio-monitor was assessed by evaluating MAI values. Thus, cadmium, copper, lead and zinc concentrations were assessed in washed and unwashed leaves of *F. retusa* collected in a contaminated area (Constantine, city, NE-Algeria). The metal concentrations of Pb and Zn were above natural limits, and MAI values were relatively high. Higher is MAI, better is plant for planting in the highest contaminated areas of a city. Thus, *F. retusa* is highly recommended for the biomonitoring of Cd, Cu, Pb and Zn in urban environment. It can also be suggested for plantation, not only from view of green-belt development, but also remediate heavy metal contaminated areas. In addition, information on plant response to HMs is useful to assess and monitor the potential risks to wildlife upon incorporation of these elements through the food chain.

Declarations

Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Availability of data and materials:

- The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

- All data generated or analysed during this study are included in this published article

Competing interests: The authors declare that they have no competing interests

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Authors' contributions:

Sahli Leila: collected and prepared samples for analysis, performed analysis (heavy metals extraction and physic-chemical characterization), statistical analysis, wrote the paper.

Belhiouani Hadjer: Heavy metals measurements, data analysis, wrote the paper.

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Figures

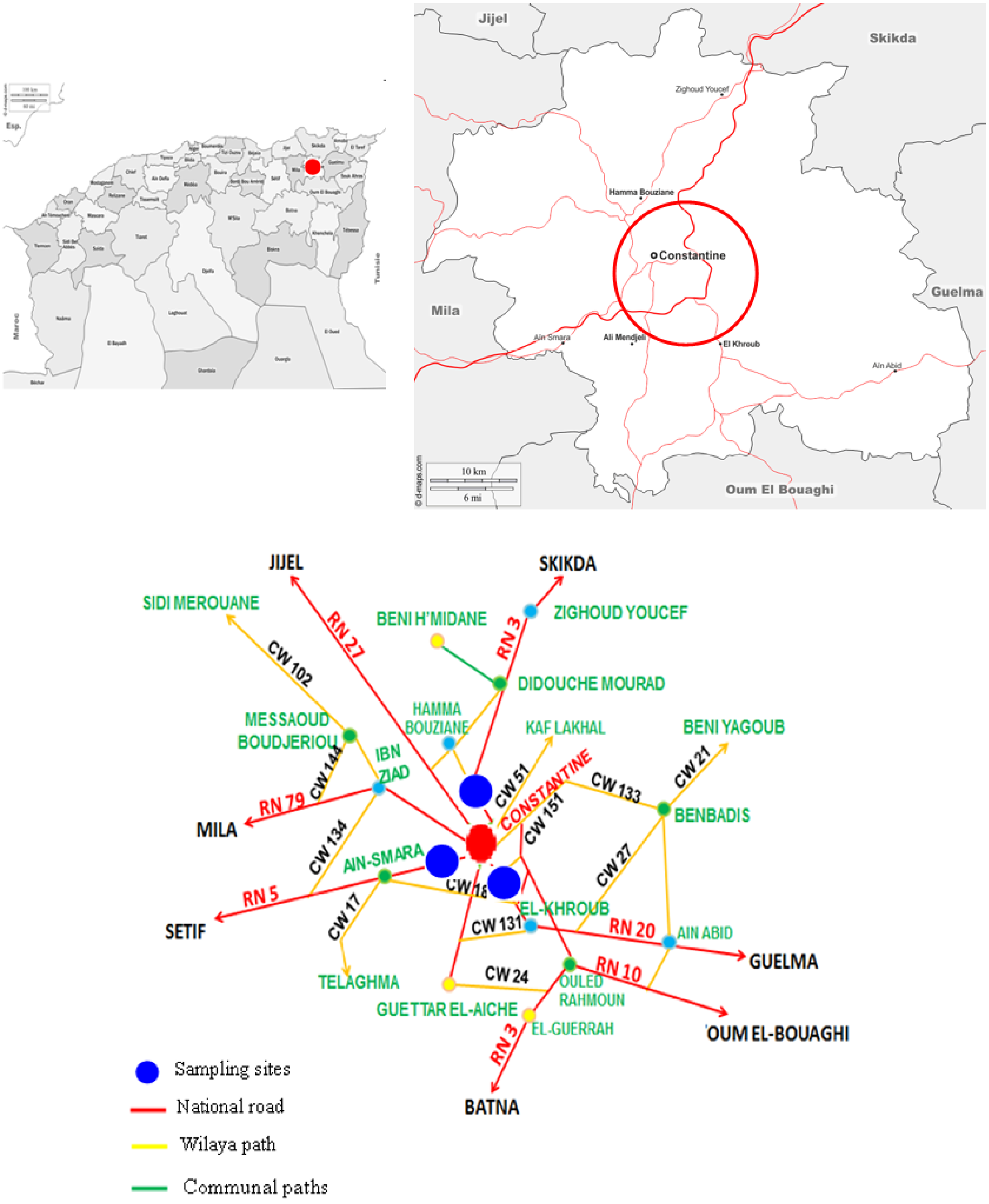

Figure 1

Road network in Constantine city and sampling sites

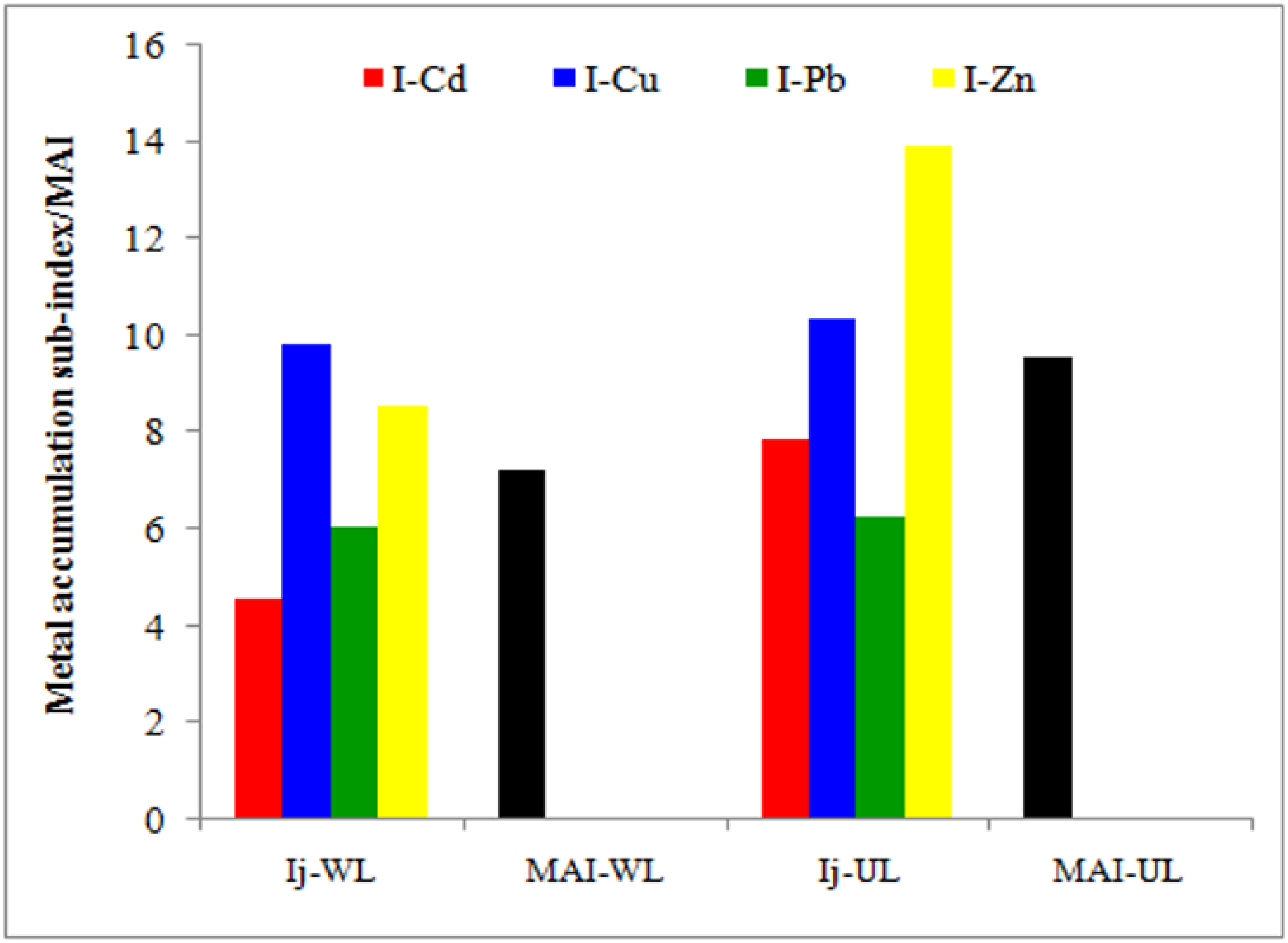

Figure 2

Metal accumulation sub-index and MAI (■) for washed leaves (WL) and unwashed leaves (UL) of F. retusa from the study area