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# Air pollution mitigation and carbon uptake of some evergreen plant species

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# Introduction

## Air pollutants and their effects on human health

In 2012, 51% of the worldwide population was living in cities and this percentage is expected to increase up to 60% by 2030 (Population Reference Bureau, 2012). Urban ecosystem is strongly unbalanced in terms of energy and matter consumption, and production of pollutant emissions and carbon dioxide ($CO_2$). $CO_2$, although not considered a pollutant, is the main greenhouse gas, responsible of the greenhouse effect with the consequent increase of air temperature (Kiran and Kinnary, 2011). Air pollution continues to pose a significant threats to health worldwide. The negative effects on human health are mainly related to the respiratory and circulatory systems (WHO, 2006; COMEAP, 2010; EPA, 2011) and they were estimated to cause more than 3.7 million deaths per year (WHO, 2012). Traffic, building heating and industrial activities are the main sources of air pollution, releasing in the atmosphere high quantities of particulate matter (PM), (Suzuki, 2006; Oliva and Espinosa, 2007; Sawidis et al., 2011). Particulate matter is a mixture of solid and liquid substances, heavy metals, black carbon, polycyclic aromatic hydrocarbons (PAH) and other substances suspended in the atmosphere (Bell et al., 2011). Usually, PM is classified based on the diameter of the particles as PM10 or coarse (2.5– 10 µm), PM2.5 or fine (0.1–2.5 µm), and PM0.1-0.2 or ultrafine (≤0.1 µm) (Beckett et al., 1998). This classification is based on the different effects on human health, which are caused by different size particles . In particular, PM10 is also defined "thoracic fraction" because is able to penetrate until the first part of the respiratory system, whereas PM2.5 presents a higher hazard because can reach the deeper parts of the respiratory system as the non-ciliated ones (Di Menno di Buccianico et al., 2006). Particles are generated from primary or secondary sources. Primary sources are the incomplete combustion of fuel, mining, quarrying, brake and tyre wear in motors and natural dusts. Combustion produces mainly PM2.5 whilst the mechanical processes generally release larger particles (PM10). Natural sources as volcanic eruptions, wind-blown dust, sea salt and biological particles such as pollen and fungal spores are also considered as primary sources. These particles often exceed 2.5 µm in size. On the other hand, chemical reactions, gas condensation, and sulphate and nitrate aerosols are responsible of secondary particles formation in the atmosphere. Particles from these sources are usually smaller than 2.5 µm (Bealey et al., 2007). Constituents and sources of PM10 and PM2.5 are reported in Table 1 and 2.

Table 1. Constituents and sources of PM10 (EPA, 2002).

| Pollution (Species) | Sources | | | |
|---|---|---|---|---|
| | Primary | | Secondary | |
| | Natural | Anthropic | Natural | Anthropic |
| Minerals | Rock erosion | Volatile dusts, roads, agriculture | - | - |
| Metals | Erosion, Organic residues | - | - | - |
| Ions | Marine spray | Salt scatter | - | - |
| Organic C | - | Asphalt and tires wear | - | - |
| Organic residue | Plant and insect fragments | - | - | - |
| Bio-aerosol | Pollen, fungi, spores | - | - | - |

Table 2. Constituents and sources of PM2.5 (EPA, 2002).

| Species | Sources | | | |
|---|---|---|---|---|
| | Primary | | Secondary | |
| | Natural | Anthropic | Natural | Anthropic |
| $SO_4^{2-}$ | Marine spray | Fossil fuels | $SO_2$ and $H_2S$ oxidation from volcanos and fires | $SO_2$ oxidation from fossil fuels |
| $NO_3^-$ | - | Vehicles, combustions | $NO_x$ oxidation from soil, fires and light | $SO_x$ oxidation from fossil fuels |
| Minerals | Rock erosion | Fugitive dusts, roads, agriculture | - | - |
| $NH_4^+$ | - | - | $NH_3$ emissions from wild animals | $NH_3$ from farms, wastewater, fertilization, vehicles |
| Organic C | Forest fires | Wood combustion, vehicles, tires wear, industries | Terpenes oxidation, fires | Hydrocarbons oxidation from vehicles and wood combustion |
| Elementary C | Forest fires | Wood combustion, vehicle emissions, | - | - |

| | | | | |
|---|---|---|---|---|
| | | industries | | |
| Metals | - | Fossil fuels, metallurgy | - | - |

Air pollutants threat mainly the respiratory and circulatory system. The effects of PM (PM10, PM2.5), ozone ($O_3$), carbon monoxide (CO), nitrogen oxides ($NO_x$) and sulfur dioxide ($SO_2$) on human health are reported in table 3.

Table 3. Human health effects of five air pollutants (EPA, 1999; WHO, 2006).

| Species | Effect on human health |
|---|---|
| PM (PM10, PM2.5) | Mortality, bronchitis (chronic and acute), asthmas, respiratory illness, shortness of breath, respiratory symptoms, restricted activity days, neonatal mortality, changes in pulmonary function, chronic respiratory diseases (other than chronic bronchitis), altered host defense mechanisms, cancer, cardiovascular disorders. |
| Ozone ($O_3$) | Respiratory symptoms, restricted activity days, respiratory restricted activity days, asthma attacks, mortality, increased airway responsiveness to stimuli, inflammation in the lung, chronic respiratory damage, premature aging of the lungs, acute inflammation and respiratory cell damage, increased susceptibility to respiratory infection, non-asthma respiratory emergency, cardiovascular disorders. |
| Carbon monoxide (CO) | Behavioural effects, cardiovascular effects, developmental effects, decreased time to onset of angina, non-asthma respiratory emergency, cardiovascular disorders. |
| Nitrogen oxides ($NO_x$) | Respiratory illness, increased airway responsiveness to stimuli, chronic respiratory damage, premature aging and inflammation of the lungs, increased susceptibility to respiratory infection, acute inflammation and respiratory cell damage, non-asthma respiratory emergency, cardiovascular disorders. |
| Sulfur dioxide $SO_2$) | In exercising asthmatics: (chest tightness, shortness of breath or wheezing), changes in pulmonary function, respiratory symptoms in non-asthmatics, non-asthma respiratory emergency, cardiovascular disorders. |

Particulate matter 2.5 often contains a specific class of organic compounds known as PAHs (polycyclic aromatic hydrocarbons). Some species of this class are fluorantrene, pyrene, chrysene, benzoantracene, benzofluorantrene, benzopyrene, dibenzoantracene, dioxins and furans which have gained particular attention due to their genotoxic and carcinogenic properties (Gies et al., 2007; Kao et al., 2007;  Lewtas, 2007; James et al., 2012). Nitro- and amino-PAH derivatives can also induce pro-inflammation responses (Øvrevik, 2010; Podechard, 2010). The PAHs are present in the combustion emissions (Totlandsdal et al., 2014), and thus traffic in the urban areas may represent the main source. These substances are low volatile and persistent in the environment and in the organism especially in the lipid tissues. Other substances as benzene, which originate from the same source, are not able to form PM due to their low vapor pressure (Grosjean and Seinfeld, 1989). Lead, Cd, Hg, and As are the heavy metals (HM), present in PM, which are associated to the main threats to human health (Hellström et al., 2001). The effects of these metals have been extensively studied. The damages caused by each of these metals are summarized in table 4.

Table 4. Effects on human health of the principal heavy metals.

| Heavy metal | Effect on human health |
|---|---|
| Cadmium (Cd) | Acute pulmonary effects and deaths (Seidal et al., 1993; Barbee Jr et al., 1999), kidney damages (Järup et al., 1995), kidney stones, skeletal damages (Järup et al., 1998), chronic renal failures (Hellström et al., 2001), osteoporosis and fractures (Staessen et al., 1999), cardiovascular mortality (Nishijo et al., 1995), probable carcinogenic effects (IARC, 1993). |
| Inorganic mercury (Hg) | Lung damages, neurological and psychological symptoms (tremor, changes in personality, restlessness, anxiety, sleep disturbance and depression), kidney damages, proteinuria, allergy, eczema (Järup, 2003). |
| Organic mercury (methyl mercury- $CH_3Hg^+$) | Nervous system damages (parestesias and numbness in the hands and feet, coordination difficulties and concentric constriction of the visual, auditory symptoms), (Weiss et al., 2002) death, (Berglund et al., 2001), coronary heart diseases (Salonen et al., 1995). |
| Lead (Pb) | Symptoms related to the nervous system (headache, irritability, abdominal pain), sleeplessness, restlessness, behavioral disturbances, learning and concentration difficulties in children, lead encephalopathy, memory deterioration, prolonged reaction time and reduced ability to understand, reduced nerve conduction velocity, reduced dermal sensibility, anemia, diminished intellectual capacity, proximal renal tubular damages (WHO, 1995; Järup, 2003), kidney damages, possible human carcinogenic effects (Steenland and Boffetta, 2000). |
| Arsenic (As) | Gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems, death, bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy, encephalopathy, bladder and kidney cancer, skin cancer and other skin lesions (hyperkeratosis and pigmentation changes), lung cancer, hypertension and cardiovascular diseases, (WHO, 2001). |

Heavy metals and other elements in general are strongly associated with PM (Duzgoren-Aydin et al., 2006) and their relative content in PM increase with particle size (Li et al., 2003; Araujo and Nel, 2009). Elements are differently distributed in PM, depending on the emission types present in the considered area. High levels of As, Mo, Ni, S, Se, V, and Zn have been associated to a petrochemical plant activities in Gela, Italy, whilst Cu, Pb, Pt, Pd, Sb, and partly Zn concentrations have been closely associated with traffic (Bosco et al., 2005). Duzgoren-Aydin et al. (2006), in Guangzhou, China, found that Cd, Cu, Pb and Zn contamination of the urban environment was more severe on the industrialized side of the city than on the western side where heavy traffic and industrial activities were limited. Element distribution in PM changes also depending on particulate size. Ziemaki et al. (2003), found that, in urban area, Pb, Cd, V, and in limiting way Zn, were distributed mainly in the fine fraction of PM (PM2.5). On the other hand, Ni, Cr and Mn were equally distributed whilst Fe was present in the coarse fraction (PM10). Carbon dioxide, in addition to PM, is massively emitted by traffic, heating and cooling systems. Other gaseous, as methane ($CH_4$), chlorofluorocarbons, nitrous oxide ($N_2O$), and tropospheric ozone ($O_3$), are also considered responsible for the greenhouse effects. The physical effect of the greenhouse gaseous is the trapping of certain radiation wavelengths that increase the atmospheric temperatures. Globally, the average of air surface temperature will increase between 0.3 and 4.8 °C by 2100 (IPCC, 2013), with severe consequences on climate and environment (Appenzeller, 2000). Impacts of climate changes are often exacerbated in urban areas as compared with rural environments because of the high artificial surfaces (buildings and roads) and high concentrations of fossil fuel combustions (Nowak, 2000).

**Services and dis-services from vegetation in the urban areas**

Plants may be significant in improving air quality of urban areas and consequently the life quality of inhabitants (Beckett, et al., 2000; Nowak, 2000). In details, the different effects that vegetation may have on the urban environment are:

- Improvement of air quality by air pollutant reduction (i.e. adsorption of particulate pollutants and absorption of gaseous pollutants).
- Beneficial influence on microclimate conditions related to the mitigation of high air temperature (Rosenfeld et al., 1998).
- Positive influence on the energetic consumption of buildings: (1) tree shading reduces the energy request on summer, (2) wind speed reduction reduces the dispersion of heat during the winter season (Heisler, 1986).

- Influence on carbon balance as a consequence of: (1) $CO_2$ emissions reduction (see previous point), (2) $CO_2$ sequestration from the atmosphere and assimilation in vegetal metabolism (Nowak et al., 2013).
- Interception of the humid deposition: pollutants which are dissolved in the rain water can be absorbed by roots once in the soil; this process reduces the dispersion of pollutants in the environment.

In particular, against air pollutants, vegetation acts as a filter able to reduce the flux of air pollutants by the interruption of the way source-target. The phenomena involved in the mitigation of air pollution by plants are through physical and chemical processes:

- adsorption or deposition on the leaf or branch surface (solid pollutants);
- absorption via stomata (mainly gaseous pollutants and $CO_2$);
- assimilation (mainly gaseous pollutants and $CO_2$ );

Adsorption is the process quantitatively more important for the reduction of solid pollutants as PM and all its components (as ex. heavy metals). Leaf surface is the part of plants mainly involved in the deposition of solid pollutants. The absorption of pollutants regards mainly gaseous substances as $NO_2$, $SO_2$ and PAHs. These substances can penetrate inside the tissues of plants by stomata and can be assimilated in the plant metabolism. In some cases, they can also cause toxicity with consequent damages to the vegetal cells and resistant species should be chosen to avoid the aforementioned phenomena and increase the mitigation efficiency of plants (Rai and Kulshreshtha, 2006). $CO_2$ sequestration depends on the photosynthesis process in which $CO_2$ is absorbed from the atmosphere and assimilated by the plant through the sugar metabolism. This contribute to decrease $CO_2$ concentration (Kiran and Kinnary, 2011; Nowak et al., 2013). Trees in urban areas con also present some negative aspects related to their secondary metabolism. Carbon allocated to the metabolism can be used by plants to produce volatile organic compounds (VOCs) which are mainly molecules of secondary metabolism, for example for the defense against insects and diseases, or for the attraction of pollinating insects. VOCs can increase the near ground ozone formation when NOx are present (Schollert et al., 2014). VOCs production involves a minor quantity of carbon as compared to the global carbon cycle, even though the impact on air chemistry and quality (ozone concentration at ground level) is large (Brilli et al., 2014). Among the VOCs, isoprene is the compound mainly released in the atmosphere by several plant species. Tree species are characterized by different productions of VOCs (Chang et al., 2012), thus attention should be paid in choosing the lower VOCs emitter plants for plantation in urban areas.

*Pollution deposition on plant surface*

Plants have been proposed as sinks against air pollution (gaseous and solid), thanks to their activity of air filtering accomplished by the leaves and bark (Fowler et al., 1989; Broadmeadow and Freer-Smith, 1996). Plants capture PM mainly through physical impaction while gaseous pollutants are captured by transpiration process (Nowak et al., 2000; Bealey et al., 2007). The presence of particulates on leaf surface is temporary because part of these can be re-suspended by wind or washed-off by rain (Nowak et al., 2000). Screening of plant species, both trees and shrubs, for their capacity in capturing air pollutants was performed in several studies (Dzierzanowski et al., 2011; Sawidis et al., 2011; Sæbø et al., 2012). Regarding the capacity of mitigation of air pollution, species specific characteristics like vegetation structure, plant height, leaf surface, leaf area index and leaf microstructure as hair or trichomes on leaves, may be important (Fowler et al., 2003, Räsänen et al., 2013). Generally, it was observed that trees had a major efficiency in capturing PM, due to their large leaf areas that creates more turbulent mixing of air passing over the plants than what observed in shorter vegetation (Fowler et al., 1989; Beckett et al., 2000). Among tree species it was observed that conifers, due to their smaller leaves and more complex shoot structures, presented a higher efficiency than broad leaf trees in capturing PM (Freer-Smith et al., 2005). In addition, evergreen plants, in general, intercept air pollutants also during the winter season due to the persistent presence of leaves. On the hand, the prolonged exposition of leaves can cause lower resistance to pollutants. Even if the potential of trees in air pollution mitigation is higher than shrubs, it was observed that, in some cases, trees can act a worsening of the air quality by the reduction of air circulation (Salmond et al., 2013). In the aforementioned study it was observed that, in street canyon, an extended tree cover can hinder the upward flux of emissions (as example the cars emissions) and the downward flux of clean air. Similar results were observed also by Buccolieri et al. (2009), in an experiment in wind tunnel on the effect of a avenue-like tree planting on air particles deposition on leaves. They confirmed that the pollution increases at the leeward wall and moderately decreases near the windward wall. Micrometeorological approaches and modeling at regional scale assessed and quantitatively estimated these beneficial effects of vegetation on urban environment (McPherson, 2007; Nowak and Crane, 2002) even if these aspects are often disregarded (Nowak et al., 2013). The phenomena of deposition of pollutants on the plant surface are defined as “Dry deposition”. Dry deposition represents all cases where particles are deposited directly onto terrestrial surfaces by gravity or following turbulent transfer vertically to the boundary layer and capture by vegetation. The other way of removing pollution from the atmosphere are classified as “wet depositions” which are pollutants deposited with rain, snow or mist (particularly windblown aerosols), (Fowler, 1984). Deposition velocity ($Vd(z)$) is a quantity used to describe the rate of dry deposition. The formula is $Vd(z) = f\chi^{-(z)}$ where $f$ is the air flux to the surface (as example the leaf surface), and $\chi$ is the concentration of the pollutant in the air at height ($z$), that usually is 1 meter (Fowler et al., 2003). Deposition velocity depends on the type of pollutant (size and chemical characteristics), nature of the surface (rough or smooth) and wind speed (National Power and CERC, 2009). Unit of measure of $Vd(z)$ is mm $s^{-1}$. Considering particles with diameter larger than 0.1 μm, it was demonstrated that deposition velocity increased with an increase in particle size. Larger particles have an higher inertia, which cause them to fall out of the air flow, permitting them to collide with the leaf surface and deposit on them (Fowler et al., 2003). A confirmation of that aforementioned is that ultra-fine particles are able to stay suspended for a longer time and can drift longer distances from the source as compared to the greater particles. High concentration of pollutant ($\chi^{z}$) tends to increase the uptake of particles by plants (Freer-Smith et al., 2005). It was also observed that impaction of particles was greater at increase in wind speed (Beckett et al., 2000). This also was explained by the larger inertia which PM assumes at high wind speed (Buccolieri et al., 2009). Considering what reported, vegetation should be placed in adequate quantity in proximity of the source of pollution where the concentration of pollutant is higher. On the other hand, this should be designed so as to avoid a marked reduction of wind speed which would cause local increase in concentration of air pollutants. More focus should be paid on the study of plant design and their effects on the capacity of mitigation. Several aspects of interaction between plants and pollution were examined as the relative species capacity, the aerodynamic interaction between plants and pollution, the estimation of the accumulation capacity etc. It is assumed that plants generally improve the air quality (Kenney, 2001; Nowak et al., 2006; Singh and Tripani, 2007), but there is still a lack of knowledge on how much these benefits on air pollution are affecting air quality and the quality of life of people. These question are mainly motivated where the unbalance between green areas (also potential green areas) and emissions is high.

*Carbon dioxide sequestration*

Plants, by the photosynthesis process, fix the carbon of $CO_2$ and allocate it to metabolism or new tissue growth (Chapin et al., 1990; Herms and Mattson, 1992). Given these characteristics, urban forests can play a critical role in contrasting increasing levels of atmospheric carbon dioxide (Nowak and Crane, 2002; Bertin, 2006; McPherson, 2007). A tree in urban area is able to reduce $CO_2$ as 3-5 trees in forest of similar size (Akbari, 2002). The carbon sequestration of urban trees was investigated by several studies and for extended areas. Nowak et al. (2013) estimated that the total tree carbon storage in U.S.A. urban areas was 643 million tonnes and the annual sequestration was estimated at 25.6 million tonnes. In addition to direct tree storage, was estimated that urban soils store approximately 1.9 billion tones, three times more than trees (Pouyat et al., 2006). The shading of tall trees on buildings during summer reduces the energy consumption for cooling. On the other hand, the reduction of wind speed during winter reduces the loss of heat. The capacity of plants in $CO_2$ assimilation and emission changes depending on tree species, age and well-being of plants. Young plants are able to allocate a higher quantity of $CO_2$ in growth compared to old plants. The health of plants is also important for this purpose. The management of urban green, the harvesting and the kind of utilization of biomass can also influence the balance between the $CO_2$ stored by plants and that released by human activities (Nowak and Crane, 2002). Plants, which request a numerous quantity of operative interventions, tend to reduce the benefits on $CO_2$ because of the consumption of fuels. Not secondary are the costs of management of trees in urban areas, even if these last are largely overcome by the benefits brought by green to the population (Soares et al., 2011). In the previous cited work, it was estimated that, in the city of Lisbon, trees cost annually $1.9 million and the value of services (energy savings, $CO_2$ reduction and air pollutant deposition) was estimated to be $8.4. There is still a lack of detailed knowledge on the real balance of $CO_2$ regarding all the cycle (from the nursery to death) of a tree in urban area. Life cycle analysis could be a useful tool to better understand the real influence of urban greening on $CO_2$ concentration.

It appears fundamental to define with precision the role and the effects of vegetation in the urban environment, in particular the PM and $CO_2$ scavenging abilities. As reported by Bealey et al. (2007), public administrations should be plan an increase of the green urban areas at every increase of the emissions. Examples of this kind of planning already exist for $CO_2$ emissions ("Million Trees NYC" project). A major attention should be given at PM emissions.

## Aims and chronological sequence of the experiments

The research projects carried out within the P.h.D activities were aimed to characterize evergreen species for their capacity in mitigation of some air pollutants and $CO_2$ assimilation. In addition, in each experiment different aspects of air pollution were investigated as follows: 1) the capacity of mitigation of different species, 2) the interaction of pollutants with meteorological parameters, 3) the trend of the concentration of pollutants on plants during the time and 3) the distribution of pollutants from the source to the neighboring area.

In Paper I, different experiments on six evergreen shrub species (*Viburnum tinus subsp. lucidum* L., *Viburnum tinus subsp. tinus* L., *Arbutus unedo* L., *Photinia x fraseri* Dress., *Laurus nobilis* L., *Elaeagnus x ebbingei* L., *Ligustrum japonicum* Thunb.) are reported. The capacity to assimilate $CO_2$ and to adsorb heavy metals (cadmium, copper, lead, nickel, zinc which) on leaf surface were investigated. The first two experiments on $CO_2$, were carried on plants in containers in 2011 and

2012. In 2011 the capacity of $CO_2$ assimilation of species under optimal water availability was evaluated. In the second experiment (2012), different measures were performed and also the effect of drought stress condition on the carbon uptake was evaluated. The third experiment, regarding the interception on leaves of heavy metals, was performed on field-grown plants, close to a heavily trafficked road. In addition to the metal adsorption of different species, the trend of presence of metals on plants during the summer season and the influence of meteorological parameters (rain, temperature, wind speed) on pollutants deposition was also studied.

In Paper II, the activities of the second year (study on the capacity of the aforementioned six evergreen shrub species in adsorption of heavy metals on leaf surface) are reported. The experiment, also in 2012, was carried out at CRA-VIV. The number of metals was extended to several other metals and elements and other changes were applied to the protocol. The aim of the experiment was to obtain more detailed information regarding the behaviour of species in the adsorption of different pollutants as compared to the results of the previous year. Also the study regarding the trend of pollutants during the summer season and their relations with meteorological parameters were studied in deep.

Paper III reports a study conducted in 2012 and 2013 during three stage periods attended at Bioforsk, Norwegian Institute for Agricultural and Environmental Research. The study was conducted on two coniferous species (*Picea sitchensis* (Bong.) Carrière and *Pinus sylvestris* L.). The experiment tested the capacity of the aforementioned species in accumulation on needles of different fractions of PM and elements, at increasing distances from an heavily trafficked road. The fact that sampling was done at different distances from the probable source of pollution (road) allowed to study the trend of distributions of pollutants which was not analysed in the previous research. In addition, the capacity of accumulation of pollutants in function of the needles age was tested.

# Paper I

Manuscript

## Carbon uptake and air pollution mitigation of different evergreen shrub species.

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**Abstract**

Seven evergreen shrub species (*Arbutus unedo* L., *Elaeagnus x ebbingei* L., *Laurus nobilis* L., *Ligustrum japonicum* Thunb., *Photinia x fraseri* Dress., *Viburnum tinus subsp. lucidum* L. *and Viburnum tinus subsp. tinus* L.), were evaluated for their ability in $CO_2$ assimilation and in leaf surface accumulation of some trace metals (except *V. tinus*). The $CO_2$ uptake and carbon allocation were determined in 2011 and 2012 in container plants under well watered and water stress conditions. The seasonal accumulation on leaf surface of Cd, Cu, Ni, Pb and Zn were measured in 2011 on plants in the ground close to a 4-lanes road. Meteorological parameters were recorded and related to foliar accumulations. Metals content in water collected at the base of plants were also measured. *E. x ebbingei* showed the highest carbon gain capacity under optimal water availability, on the contrary, under drought conditions, photosynthesis was strongly reduced. *P. x fraseri* maintained a good level of carbon assimilation also during drought. *E. x ebbingei* presented the highest trace metal accumulation at leaf level, mainly due to the higher leaf area. Meteorological conditions appeared to modify the dynamics of seasonal leaf metal accumulation. Rain and high air humidity decreased the metals on leaves whilst wind velocity and air temperature tended to increase the presence of pollutants. The water collected at the base of plants contained more trace metals

compare to the control water. In conclusion, the use of species with very sensitive photosynthetic responses to substrate moisture (*V. tinus subsp. lucidum, L. japonicum, E. x ebbingei*), is not recommended in drought-prone environments, whereas drought tolerant "mesic" species (*P. x fraseri*), should be planted to maximize carbon uptake. *E. x ebbingei* could be used in order to optimize the interception of air pollutants. Though the experiment is not conclusive, it may offer a useful insight of $CO_2$ assimilation potential and air pollution mitigation of widely used shrubs which may be applied in urban areas and roadside greening sustainable planning in southern Europe.

Key words

meteorological parameters, seasonal trend, trace metals, traffic pollution, carbon sequestration, Fv/Fm, RGR.

**Introduction**

Human activities as traffic, industry and heating are contributing to change the atmospheric environment in terms of $CO_2$ concentration and air pollution (Grubler, 1994; O'Meara, 1999; Suzuki, 2006). Since the latest 1800s, an increase between 0.0-0.6 °C of the average Earth's surface temperature was verified (Nowak and Crane, 2002), and the main causes of this phenomena knows as "Global warming", were identified in the large emission of specific gases, as water vapor, $CO_2$, $CH_4$ and $O_3$, also known as "Greenhouse gases". The largest driver of global warming is $CO_2$ which is largely emitted from all the phenomena of combustion (PBL Netherlands Environmental Assessment Agency, 2013). Urban Greening have been reported to contribute effectively to $CO_2$ uptake and storage, as $CO_2$ is converted into organic carbon by photosynthesis then stored as woody biomass for long-term (Pugh et al., 2012). The reason of that is because trees and shrubs are planted inside or nearby the urban environment, where the concentration of $CO_2$ and pollutants is higher (Niinemets and Peñuelas, 2007). In addition they offer benefits *in situ*, being appreciated by over half of the world population (McCarthy et al., 2010). Plant species differ in their relative capacity to assimilate and store $CO_2$ (Somogyi et al, 2008; Semwal et al., 2013). Previous research investigated $CO_2$ storage by several trees species, and found that $CO_2$ storage is positively related to tree life span and size at maturity (Nowak et al., 2002). On the other hand, the potential of shrubs for $CO_2$ storage has been poorly investigated, despite they can account for about 10–11% of the total carbon storage and for 21–25% of total annual carbon uptake of the urban vegetation (Jo and McPherson, 1995). In Mediterranean areas, the use of drought tolerant shrubs, could be a considerable help to the local carbon sequestration (Bombelli and Gratani, 2003). There is urgent need thus, to assess the potential for $CO_2$ uptake of widely used shrub species. Particular interest should be given in determining which species maintain a good $CO_2$ assimilation during drought, as main stress in the Mediterranean urban climate (Bussotti et al., 2013; Fini et al., 2014). So the use of shrubby species is suggested as a valid complement especially where there is not enough space for a tree. In parallel to $CO_2$ assimilation and carbon storage, plants may play a role in decreasing the local air pollution. Particulate matter (PM) is the principal component of anthropogenic air pollutants that includes a mixture of elements, heavy metals, black carbon, polycyclic aromatic hydrocarbons and other substances suspended in the atmosphere (Bell et al., 2011). Elevated levels of heavy metals are common in urban areas as results of both a wide range of human activities and natural processes (Lu et al., 2010). Plant can adsorb and absorb particulate and gaseous pollutants (Nowak et al., 2000; Nowak et al., 2006; Bealey et al., 2007) and different species were evaluated for their capacity of capturing air pollutants (Sawidis et al., 2011; Dzierzanowski et al., 2011; Sæbø et al., 2012). Leaf surface is a temporary retention site for pollutants which presence is influenced by meteorological factors (Nowak et al., 2006). Heavy metals are strongly associated with PM (Duzgoren-Aydin et al., 2006), especially with the coarse fraction with diameters up to 10 µm ($PM_{10}$) (Araujo and Nel, 2009). Anicic et al. (2011), found a seasonal accumulation, in May and in September of Cr, Fe, Ni, Zn and Pb on leaves of *Aesculus hippocastanum* and *Tilia spp.* More detailed information should be available regard the trend of metal and element deposition during a season and related to weather conditions in a dry and warm area, like for example Italy. Most of the research in the last 15 years was carried out on temperate tree species (Beckett et al., 2000; Nowak et al., 2002; Nowak and Crane, 2002; Pugh et al., 2012). However, knowledge on shrubby evergreen species, commonly used in urban green areas of southern Europe, is lacking and research should focus more on shrubs since these have been shown to have a significant contribution to air pollution mitigation and carbon uptake (Jo and McPherson, 1995; Bombelli and Gratani, 2003; Sæbø et al., 2012). In addition evergreen plants are able to intercept air pollutants also during the winter season (Freer-Smith et al., 2005), when the highest concentration of air pollutants is found (Pikridas et al., 2013). Not secondarily, in street canyons, threes can worse the concentration of pollutants at the pedestrian level, by the reduction of air circulation (Buccolieri et al., 2009; Salmond et al., 2013). The experiment 1 and 2 were thus aimed at identifying $CO_2$ uptake and storage of seven shrub species (*Viburnum tinus subsp. lucidum* L. cited as *Viburnum lucidum*, *Viburnum tinus subsp. tinus* L. cited as *Viburnum tinus, Arbutus unedo* L., *Photinia x fraseri* Dress., *Laurus nobilis* L., *Elaeagnus x ebbingei* L., *Ligustrum japonicum* Thunb.), grown under optimal water availability (exp. 1) or under drought stress (exp. 2). The aims of the experiment 3 were: 1) to identify the best species, among the aforementioned evergreen shrub species (*Viburnum tinus* was not included), in accumulating trace metals (Cd, Cu, Ni, Pb and Zn), on leaf surface; 2) to study the relations between trend of metals pollutants on leaves and the meteorological conditions outside.

**Materials and Methods**

**Experiment 1: Carbon uptake and storage under optimal water availability**

In autumn 2011, 84 uniform, two-year-old plants (12 per species) of *Arbutus unedo*, *Elaeagnus x ebbingei*, *Laurus nobilis*, *Ligustrum japonicum*, *Photinia x fraseri*, *Viburnum lucidum* and *Viburnum tinus*, were potted into 3-L containers. The substrate was a peat: pumice mixture (4/1, v/v) added with 3 kg/m$^3$ of a controlled release fertilizer (Osmocote Exact, 18-2,5-7, 8-9 months, Everris, Intl. B.B, Geldermalsen, NL). Plants were grown outside under full sunlight, and irrigated daily to container capacity to avoid any water stress until the end of the experiment. Plants were arranged in a randomized block design with 6 blocks and 2 plants per species in each block. Daily trend of net photosynthesis, transpiration and water use efficiency was measured for twelve days in summer 2011, between 09.00 a.m. and 06.30 p.m., using an infrared gas analyzer (Ciras 2, PP-system, Amesbury, MA). Measurements were conducted at 380 ppm and ambient irradiance on 18 current season fully expanded leaves per treatment. Daily carbon gain was calculated by integrating the daily assimilation curve (Fini et al., 2012). In April and November 2011, 72 plants (one plant per block, treatment, and species) were harvested for biomass measurement. Plants were cut at the root flare and roots were cleaned from the medium with a flush of air. Leaves were separated from stems and scanned with an A3 scanner. An image analysis software (Image Tool 1.3, UTHSCSA) was used to measure leaf area. To determine dry weight leaves, stems and roots were oven-dried at 70°C until constant weight was reached (≈72 h). Root-to-shoot ratio was calculated as the ratio between root dry weight and leaves + stem dry weight (Fini et al., 2011). Finally, whole-plant carbon uptake was calculated from net photosynthesis per unit leaf area and total leaf area per plant.

**Experiment 2: Carbon uptake and storage under drought stress**

In March 2012, 144 three-year-old plants of the same species previously described (24 plants per species; *Laurus nobilis* was not used), were potted in 5-L containers. Substrate and fertilization were the same as in exp. 1. Plants were arranged in a randomized block design with 3 blocks and 8 plants per species in each block. All plants were daily watered at container capacity until August and then exposed to water stress according to the following treatments: 1) WW: 72 plants (4 plants per species per block) were daily watered at container capacity throughout the experiment; 2) WS: water was withheld to 4 plants per species for two periods of 5 days (drought phase 1 and 2), separated by 14 days of partial relief. During the partial relief the substrate moisture was maintained at 30% of cc, corresponding to a mild to moderate drought (Ruiz-Sanchez et al., 2000; Fini et al., 2011) (Fig. 2A). Substrate moisture was determined using a gravimetric method (Sammons and

Struve, 2008). Significant physiological parameters were measured 6 times during the 24 days of the water stress experiment. These included: 1) leaf gas exchange, measured at T-0 (before the onset of drought), T-1 (1 day after the imposition of drought), T-2 (3 days after the imposition of drought), T-3 (5 days after the imposition of drought), T-4 (end of partial relief), T-5 (end of the experiment), as in the experiment 1; 2) pre-dawn water potential, measured at T-3 using a Scholander type pressure bomb (PMS Instruments, Albany, OR) between 03.00 a.m. and 05.00 a.m.; 3) maximum quantum yield of PSII photochemistry (Fv/Fm); 4) chlorophyll *a* fluorescence induction (OJIP) curve; 5) drought-induced changes in growth rate were measured as RGR as described in experiment 1. Points 3 and 4 were measured simultaneously as leaf gas exchange as described in previous works (Fini et al., 2011; 2013).

**Experiment 3: Leaf surface accumulation of trace metals**

In Autumn 2010, 50 three-years-old plants of *Arbutus unedo, Elaeagnus x ebbingei, Laurus nobilis, Ligustrum japonicum, Photinia x fraseri* and *Viburnum lucidum* (300 plants in total), were planted in the field, in a tilled soil, along a 4-lanes high traffic principal road (“Francesca vecchia”) (N 43° 52' 57.7992", E 10° 40' 58.0692") in Pescia (Tuscany, Italy). Plants were planted parallel to the road to form 2 vegetation belts 30 m long and 5 m wide each, starting 1.5 m from the road. Twenty-five plants per species and belt formed a 5 by 5 m section. At the moment of planting, plants were pruned to uniform size of 150 cm, with the exception of *L. japonicum* and *E. x ebbingei* which were 130 cm tall. The species were allowed to establish undisturbed for one year. Plants were irrigated as needed with a sprinkler system. Total leaf area was measured on 4 plants per species using a RS 2 XA illumination and camera system Haiser, Germany) and A3 Lightbox G.C.L., UK) with WinDIAS software (Dynamax Inc., USA). Total leaf areas per plant after cutting are shown in table 1. In 2011, leaf trace metal deposition was measured three times (June, August e October). In order to study the seasonal trend, only leaves formed in the current season were collected. Samplings were conducted after at least 10 rain-free-days. Two replicates of 10 leaves fully expanded per species, per belt (40 leaves in total), were collected including leaves from the ground level to the top of the plants. Leaf area of every sample was measured. Leaves of each species were collected at least 1.5 meters apart from the adjacent species in order to reduce the influence of the position. Leaves with pests or diseases were avoided. During the experiment, 72 samples were collected. In the laboratory, leaves were washed in 50 ml of solution composed by distilled water and HCl 0.01 M (pH 2.0), per 30 minutes taking samples on an orbital shaker. The solutions of the different samples were directly analyzed by Inductively Coupled Plasma – Optical Emission Spectrometer – Dual Vision (Optima 2000, Perkin Elmer), in order to measure concentration of Zn, Cd, Pb, Ni and Cu. The results were expressed per unit area of leaf surface. With the aim of measuring the quantity of metals washed off from the canopy by precipitations, two containers (size 50 x 100 cm) were placed at the base of four plants (replicates) per each species. Control containers were placed at the same distance from the street compared to the other containers but in areas without vegetation. Rain water was collected, measured and stored in the dark at from June to October 2011, after every significant rain event (>5 mm). In October 2011, 20 ml of rain water were homogenously taken and dried at 50°C in order to recuperate the sediments. 300 mg of dry matter were digested with 5 ml of a mixture of $HNO_3$ (65%):$HClO_4$ (68%) (5:2) v/v at 180°C per 60’ using a Heating digester DK 6, Velp® Scientifica, (Italy). Water cooling was applied at the heating digester in order to minimize the loss of metals by evaporation. The measured metal concentrations of every sample were multiplied for the total volume of collected rain water in order to obtain the total quantity of each metal washed off by rain from the canopy of every species. Height of plants and crown diameter were measured on 6 plants (3 for each belt), per species for three sampling events. Leaf area index (LAI) was also measured by a ceptometer (AccuPAR LP-80, Decagon devices, inc., WA, USA), at one meter above the ground. In October, the total leaf area of four plants (replicates) per species were measured by destructive harvests. Observations on the morphology of the leaf surface and presence of particulate matter on the abaxial and adaxial surfaces were carried out using a FEI

ESEM Quanta 200, (Fei Corporation,Eindhoven, The Netherlands), operating in low-vacuum mode (the chamber pressure was kept at 1 Torr) and 25kV. Trace metal deposition on the whole plant was then calculated by multiplying the depositions per unit leaf area and the whole plant leaf area. Meteorological parameters as air-temperature, relative humidity (RH%), precipitation and wind speed, were measured at 1.5 meters from the ground, for the entire period of sampling by a meteorological station iMetos® SD (Pessl instruments, Hanover, Germany) placed in the proximity of the trial field.

**Statistical analysis**

Growth parameters and water relations were analyzed using one-way (exp. 1) or two-ways Anova (exp. 2). Leaf gas exchange was analyzed using repeated measures Anova. The separation of means was carried out using Duncan's MRT (SPSS statistics 19, IBM Company ©, New york, US). Differences in trace metal accumulation (exp. 3), were tested with repeated measures Anova mean separation using Duncan's MRT (CoStat 6.303, CoHort Software, Monterey, CA, USA). The relationships between metal accumulation on leaves and climate parameters were tested using Partial Least Square Regression (PLSR) for each metal separately. PLSR is useful when an high level of multicollinearity among the explanatory variables is assumed (Rosipal and Trejo, 2001). Correlation between the accumulated metals was tested using Pearson product-moment correlation coefficients (r). Only the r values above 0.5 were considered. Multivariate methods were used to identify the possible sources of the different metals. Cluster Analysis (CA), was performed using the Ward’s method and Euclidean distance as metric (Oliva and Espinosa, 2007). Factor Analysis (FA), was accomplished with Varimax rotation (Lorenzini et al., 2006). The outliers were identified with scatterplots and removed from the dataset.

## Results

**Experiment 1: Carbon uptake and storage under optimal water availability**

*E. x ebbingei* followed by *L. nobilis*, had the highest carbon sequestration value (both expressed on leaf area basis and on the whole plant) when grown under optimal water availability (Fig. 1A, 1B). *P. x fraseri* performed good on leaf area basis, but whole plant uptake was limited. On the other hand *V. lucidum* and *V. tinus* showed the lower capacity of $CO_2$ assimilation. *L. nobilis* and *E. x ebbingei* showed the highest relative growth rate (Fig. 1C). A good correlation between carbon uptake and growth rate was found (Fig. 1D). Carbon allocation to leaves was higher in *V. lucidum* than in the other species, while *V. tinus*, *E. x ebbingei* and *L. japonicum* displayed to lowest C-allocation to leaves (Fig. 3).

**Experiment 2: Carbon uptake and storage under drought stress**

On average substrate moisture of WS plants declined to 15% at the end of the "withholding 1" phase (T-3), then was maintained around 30% until T-4, finally declined to 12% at the end of the "withholding 2" phase (T-5) (Fig. 2A). Drought differentially reduced the maximum quantum yield of PSII photochemistry (Fv/Fm) during the "withholding water 1" phase (Fig. 4). *L. japonicum*, *E. x ebbingei* and *V. lucidum* showed the higher depletion in Fv/Fm, whereas *P. x fraseri* displayed the lowest deviation. In particular, Fv/Fm decreased below 0.70 in *L. japonicum* and *V. lucidum*. Carbon assimilation of WW plants was similar to values previously observed. Consistently, under optimal water availability, *E. x ebbingei* was the species showing the higher net photosynthesis (data not shown). However, as drought progressed, photosynthesis of *E. x ebbingei* was strongly reduced (Fig. 2B). Similar behavior was found in all the "mesic" species. *V. lucidum* showed a very low $CO_2$ assimilation during drought.

**Experiment 3: Leaf deposition of trace metals**

*Leaf metal and PM deposition*

Species accumulated significantly different quantities of Pb on leaf surface (Table 2). *L. japonicum*, *V. lucidum* and *E. x ebbingei* showed the highest values while *L. nobilis* accumulated the lowest amount. The quantity of Cu, Ni, Pb and Zn accumulated by the whole canopy surface was significantly higher in *E. x ebbingei* than in the other species. *L. japonicum* presented the lowest values in Cu and Ni accumulation while *L. nobilis* and *V. lucidum* in Pb and Zn respectively. Generally, the accumulation of metals increased from the first to the second period and, thereafter, decreased reaching the initial level. All the elements, with the exception of Pb, presented a significantly different accumulation between periods ($P<0.001$), (Fig. 5). The results of PLSR analysis (Table 3), with 4 significant results of 5, suggest that presence of the metals on leaves is negatively related to precipitation and RH% and is positively related to temperature and wind velocity. The observations carried out by ESEM showed the clear presence of particulate matter (PM) on the upper and lower surface of every species, the presence of trichomes in *E. x ebbingei.*

*Evaluation of metals washed off from the canopy by rain*

The rain water collected at the base of plants showed higher quantities of Zn, Cu and Pb compared to controls (Fig. 6). *A. unedo* presented high values of Cu, Zn and Pb whilst the other species were characterized by an intermediate values.

*Metal source identification using multivariate methods*

Cluster analysis (CA) grouped the metals in two principal clusters. In the first cluster were included Cu and Ni and in the second one Cd, Zn and Pb. (Table 4). Factor Analysis (FA) (Table 4), indicated that approximately 85% of the variance may be explained by the first 2 factors. Factor 1, which accounted the 58% of the total variance, showed positive loadings with Cu, Ni and Zn. In factor 2 (27% of variance), the dominant elements were Cd and Pb. Correlation analysis between metals on leaves, showed that Cd is correlated with Pb ($r = 0.51$), Cu is correlated with Ni ($r =0.92$) and Zn ($r = 0.83$) and Ni is correlated with Zn ($r = 0.77$).

## Discussion

### Experiment 1: Carbon uptake and storage under optimal water availability

The high value of carbon gain observed in *E. x ebbingei* was linked to its higher water use efficiency than the other species. The low whole uptake of *P. x fraseri* was explained by the lower leaf area compared to other species. *V. lucidum* and *V. tinus* showed a low uptake of $CO_2$ may because of the limited photosynthetic potential. High carbon uptake does not necessarily turn in high long-term carbon storage, as not all assimilated carbon is used for growth. Conversely, some carbon is allocated for the secondary metabolism, or reserve production and reproduction (Herms and Mattson, 1992). However, the correlation between carbon uptake and growth rate confirms *E. x ebbingei* and *L. nobilis* as the best species for carbon sequestration among those investigated if resources are not limiting. Results on carbon allocation gives important indication on the real potential of $CO_2$ storage of species. It must be considered that, for a given increase in plant biomass, species which invest more in leaves than in woody biomass, store carbon for a shorter period of time, particularly in the urban environment where shaded leaves are artificially removed (Nowak et al., 2002).

**Experiment 2: Carbon uptake and storage under drought stress**

The values of Fv/Fm below 0.70 found in *L. japonicum* and *V. lucidum,* indicate a severe photoinhibition, and then a stress condition of these species when water availability is not optimal (Percival et al., 2005; Kalaji et al., 2012; Fini et al., 2013). Among the “mesic” species, *Photinia x fraseri* was the species more capable of maintaining carbon assimilation during drought and to promptly recover during partial relief (T-4). On the other hand, more xeric Mediterranean shrubs as *Arbutus unedo* and *Viburnum tinus,* which showed relatively low assimilation rates under optimal conditions, were less affected by drought (Fig. 2B).

**Experiment 3: Leaf deposition of trace metals**

*Leaf metal deposition and evaluation of metals washed off from the canopy by rain*

Only Pb, among the measured metals, showed a differently amount depending on species. This fact does not permit to drawn solid conclusions about the relative ability in metals accumulation on leaves of the examined species. In addition, the species that showed the highest quantities of Pb (*L. japonicum*, *V. lucidum* and *E. x ebbingei* ), had no common specific characteristics, among the ones considered, which differentiate them with regard to the other species (Table 5, Fig. 7). *E. x ebbingei* is the only species with a visible presence of trichomes which can be related to a higher capacity of pollution capturing (Beckett et al. 2000). *L. japonicum* and *V. lucidum*, unlike the other species, showed the presence of possible glands, especially on the lower leaf surface, with a probable secreting activity (indicated by the lighter color in correspondence of glands). This could be a speculation, but the secreting activity could have increased the values of Pb in these species. The results of the whole accumulation in *E. x ebbingei* suggest that the total leaf area of the plant is more significant than the anatomical characteristics in the total capacity of plant in air pollution removal. High growth parameters as high leaf area, LAI, crown diameters and height of plant are already been linked to a higher leaf surface accumulation capacity (Bunzl et al., 1989; Beckett et al., 2000; Fowler et al., 2003; Freer-Smith et al., 2005). In addition, also the small size of leaves tends to increase the air pollution mitigation (Freer-Smith et al., 2005). Species with a fast growth rate and large and thick canopy, composed by small leaves, are better suited for air pollution mitigation. The results of the trend of metals on leaves surface agree with that reported in the literature (Nowak et al., 2006), about the temporary retention of pollutants on leaves. The results of PLS regression, especially for Cu and Zn where the $r^2$ is above 50, make possible to predict the accumulation of elements with moderate accuracy, by using the climate parameters. The inverse/negative relation between accumulation of metals and rain indicates that metals on leaves decreased at increase in rain and confirm the role of scavengers that rain plays on the leaf depositions (Nowak et al., 2006). The inverse relation between metals accumulation and RH% may be explained due to the increase which RH% causes in PM diameter. When PM are larger than 0.1 µm, an increase in diameters leads to increase the deposition velocities (Fowler et al., 2002; Litschke and Kuttler, 2008;). A reduction of PM, and related metals, which reached the plants could occur as a consequence of the high increase in deposition velocity. The positive relation of metals with wind speed could be due to the effect of increase in deposition velocities causes also by wind speed (Beckett et al., 2000). Also the increase in temperature was found to be positively related to pollution accumulation on leaves (Cavanagh et al., 2009). Given the characteristics of the protocol used for the collection of rain-water, which doesn't permit to exclude the possibilities of partial alteration of the results, were considered more the differences between species and control container rather than differences among species. The higher quantities of metals in container under plants is a further demonstration of the role of plants in capturing air pollution (Nowak et al., 2000; Bealey et al., 2007). The effect of washing off caused by rain is also confirmed. Indications may be drawn also regarding the major capacity of plants with a consistent development in height, in intercepting and accumulating air pollutants compared to grass (Fowler et al., 2003).

*Metal source identification using multivariate methods*

The results of the used multivariate methods were compared in order to identify the possible source/s of different elements. Cu, Ni and Zn have high loadings in factor 1 of FA and are all strongly correlated. In CA, Cu and Ni are clustered in a different group compared to Zn, then Zn were excluded. The relationship between Cu and Ni is then supported by three different multivariate methods. Cd and Pb are dominant in factor 2 of FA and are significantly correlated. Moreover in CA they are clustered together in the second group. Also relationship between Cd and Pb is then confirmed by three different multivariate methods. Considering these results, two different groups were created: Group 1 (Cu and Ni) and Group 2 (Pb and Cd). All the metals present in the two groups have been attributed to the traffic emissions (Pant and Harrison, 2013). On the other hand the division in two groups performed by the multivariate methods may indicate the presence of two different sources for the studied metals. Cu is largely used in Pescia due to the widespread floriculture activity. Ni is a micronutrients for plants then also its presence may be related to fertilization practices of soil (Barker and Pilbeam, 2006). On this base, Group 1 may be classified as "agricultural related group". Group 2 (Pb and Cd), can be attributable to the traffic emissions (Pulles et al., 2012). Since the aim of the research was the identification of the pollution source, it appears important to consider not only the singular metal by itself but also the relationships between different metals and the characteristics of the sampling site. Comparison of different methods makes the results more reliable.

## Conclusion

### Experiment 1: Carbon uptake and storage under optimal water availability

Under optimal water availability, *E. x ebbingei* was the species showing the highest daily carbon uptake, the highest growth rate, and the highest allocation to woody biomass. These results make this species a very promising shrub for carbon sequestration urban areas with good water availability.

### Experiment 2: Carbon uptake and storage under drought stress

Photosynthesis of some species (*V. lucidum, L. japonicum, E. x ebbingei*) was very sensitive to substrate moisture, therefore the use of these species in drought-prone environments in not recommended. On the other hand, more xeric species (*Arbutus unedo, Viburnum tinus*) or drought tolerant “mesic” species (*Photinia x fraseri*) should be planted to maximize carbon uptake in areas where water is a limiting resource.

### Experiment 3: Leaf deposition of trace metals

Ultimately it was not possible to drawn clear conclusions on the relative accumulation capacity of metals on unit leaf area of different species. However was possible to discriminate among the global accumulation capacity of every species and linked the results to a faster and higher growth of plants. Metals deposition seems to be decreased by precipitation rain and relative humidity and favorite by wind speed. The higher content of metals in the water of control containers may confirm the activity of interception of particles made by plants. The removal of deposited pollution by rain and the consequent deposition on the ground, helps to reduce the re-suspension of pollution in the air.

### General conclusion

The present experiment was aimed at evaluating the potential of some shrub species to sequester air pollutants and to store $CO_2$ from the atmosphere. *Elaeagnus x ebbingei* shown the highest carbon storage under optimal water availability, but the species were shown to be unable to thrive in drought-prone environments. If water availability is a limiting factor, other species, such as *Photinia x fraseri*, *Arbutus unedo* and *Viburnum tinus* should be preferred. Regarding the relative capacity of interception of trace metal from the air, were not obtained a clear discrimination among species because only Pb was differently accumulated on leaves. *E. x ebbingei, L. japonicum* and *V. lucidum* showed the highest unitary accumulation of Pb on leaves. On the other hand, *E. x ebbingei*, had the highest whole plant leaf accumulation of all the measured metals mainly because of a faster and higher growth. We are aware that only a limited number of species were tested here, therefore this experiment is unlikely to be a conclusive evaluation of $CO_2$ uptake potential of shrubs. This study may offer for the first time a useful insight of $CO_2$ assimilation and trace metals accumulation potential of widely used shrubs for urban green areas in southern europe.

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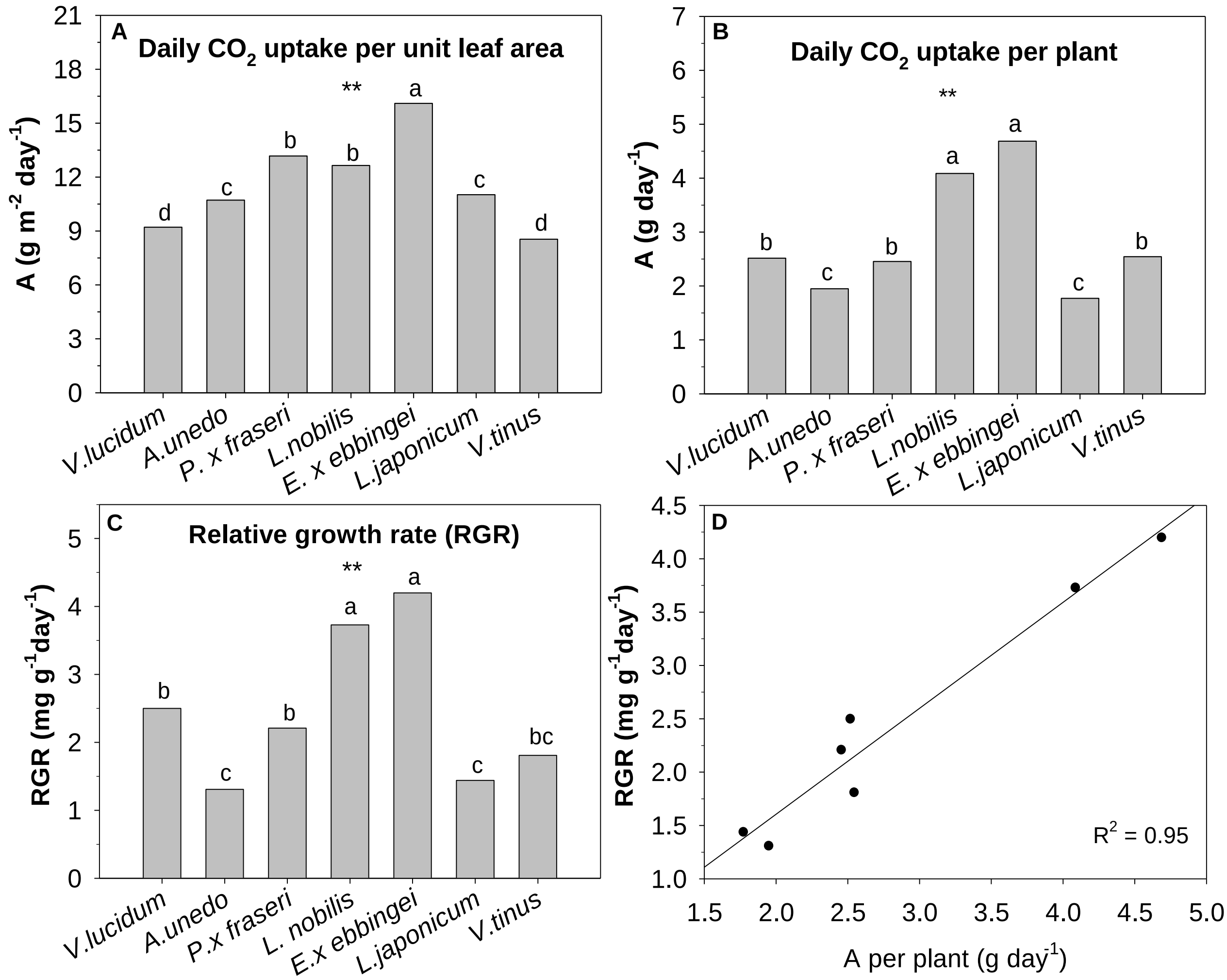


Figure 1: Daily $CO_2$ uptake per unit leaf area (A), daily $CO_2$ uptake of the whole plant (B), relative growth rate (C) and relationship between RGR and whole plant daily $CO_2$ assimilation (D) of seven different shrubs in 2011, under optimal water availability. Data of $CO_2$ uptake are the average of 12 daily measurement of net photosynthesis. Different letters indicate significant differences in RGR among species at P<0.01 using Duncan's MRT.

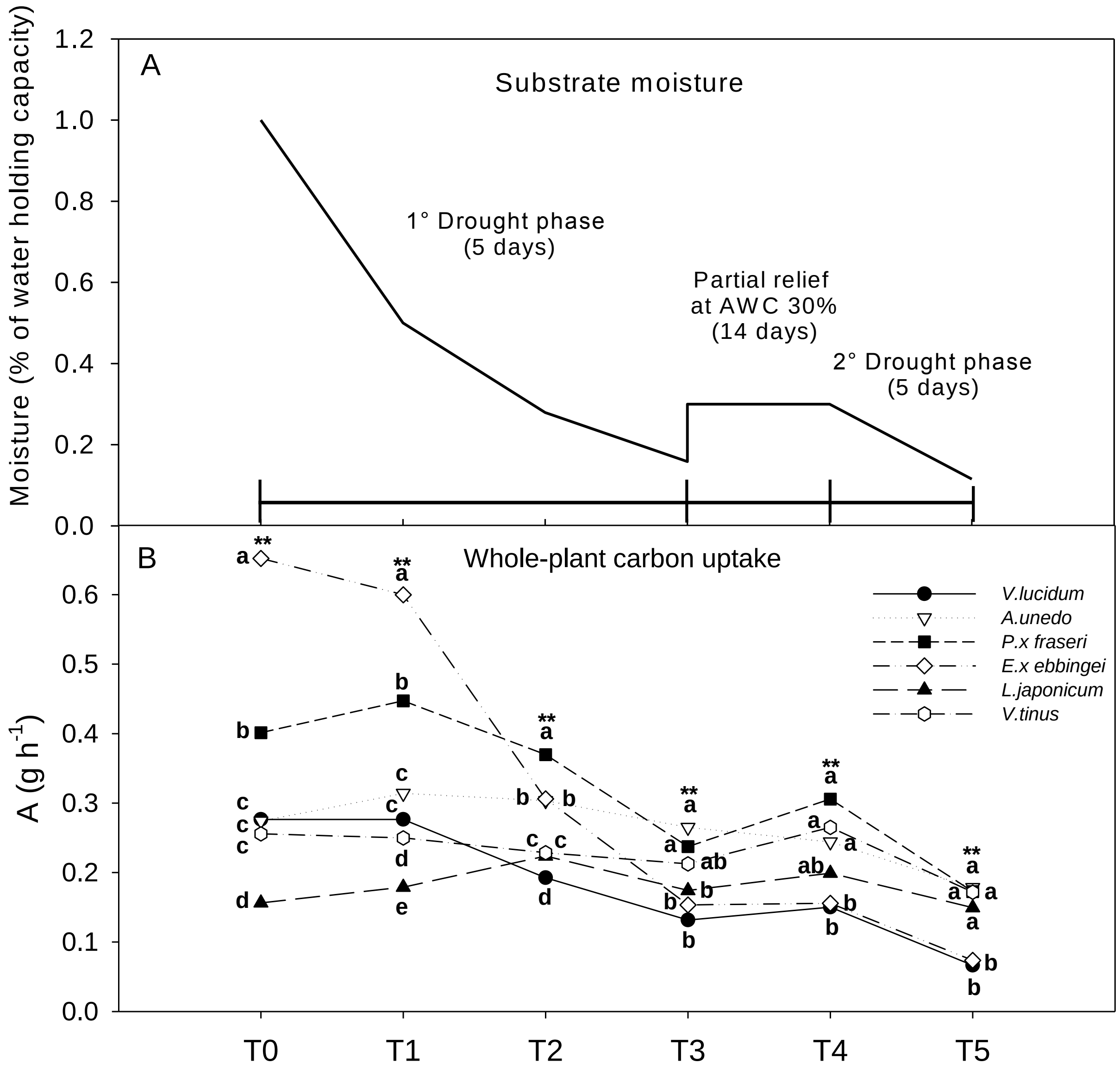


Figure 2A: Irrigation scheduling and substrate moisture (expressed as percentage of the water holding capacity of the container), for plants under drought stress (WS). Data of substrate moisture are the average of 6 species and 12 plants per species. T indicate when physiological measurements were carried out. 2B: Whole plant carbon uptake in 6 shrubs grown under water stress in 2012. Different letters within the same sampling date indicate significant differences among species at P>0.01 using Duncan's MRT.

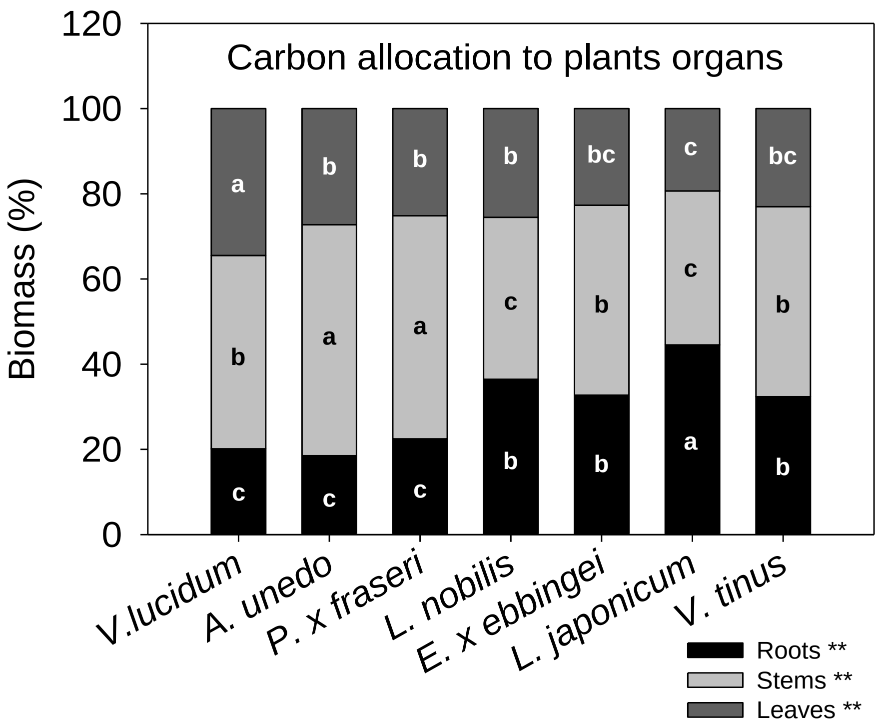


Figure 3: Carbon allocation to different plant organs in seven shrub species in 2011, under optimal water availability. Different letters within an organ (i.e. leaves. stem and roots) indicate significant differences among species at P<0.01 using Duncan's MRT.

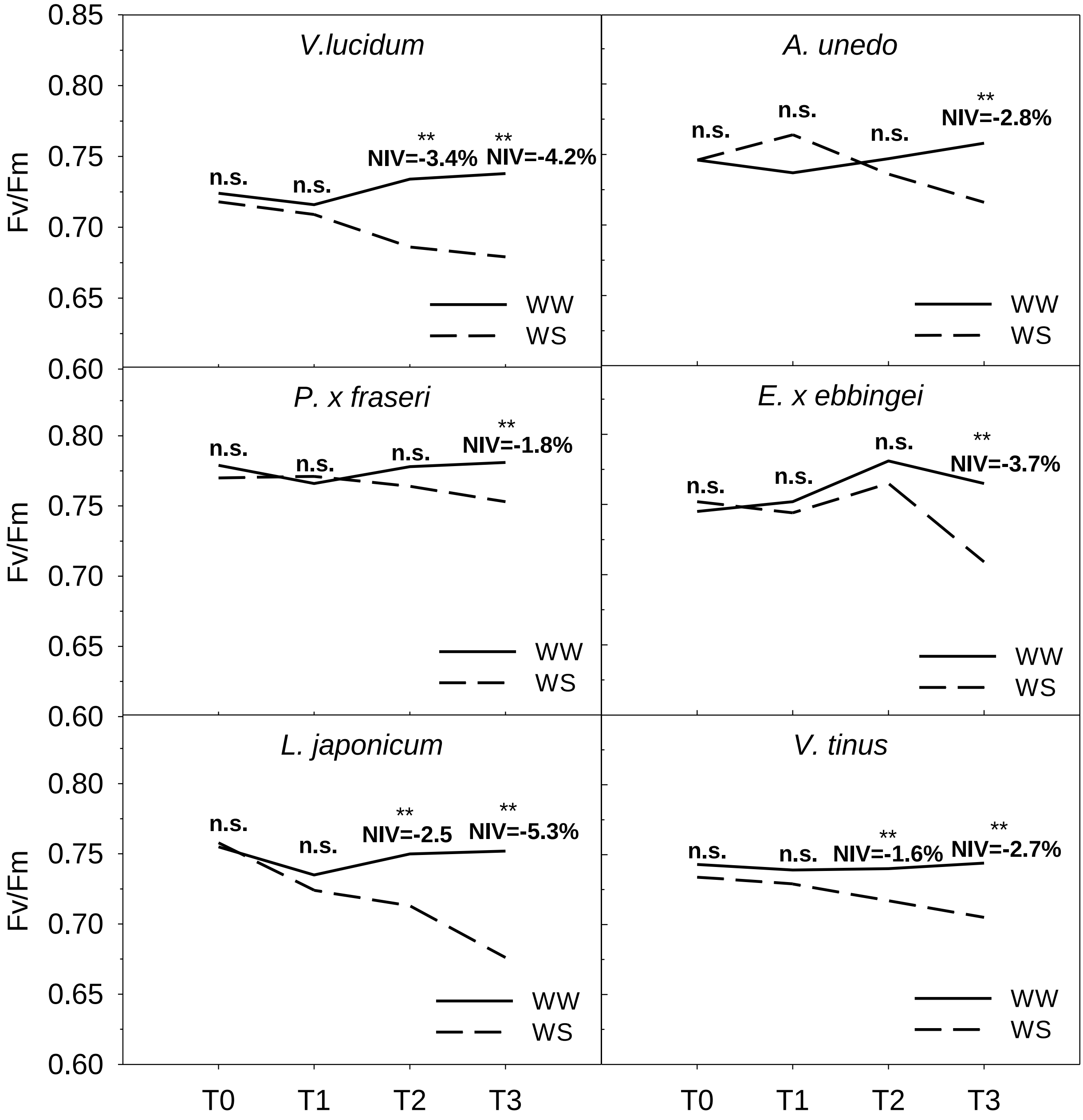


Figure 4: Maximum quantum yield of PSII photochemistry during the "drought phase 1" in 6 shrubs grown in either well watered (WW) or water stress (WS) conditions, ** indicate significant differences between WW and WS plants of a species. The normalized index of variation (NIV) was calculated as: $[(Fv/Fm)_{WS} - (Fv/Fm)_{WW}]/ [(Fv/Fm)_{WS} + (Fv/Fm)_{WW}]$ (Tattini et al.. 2006).

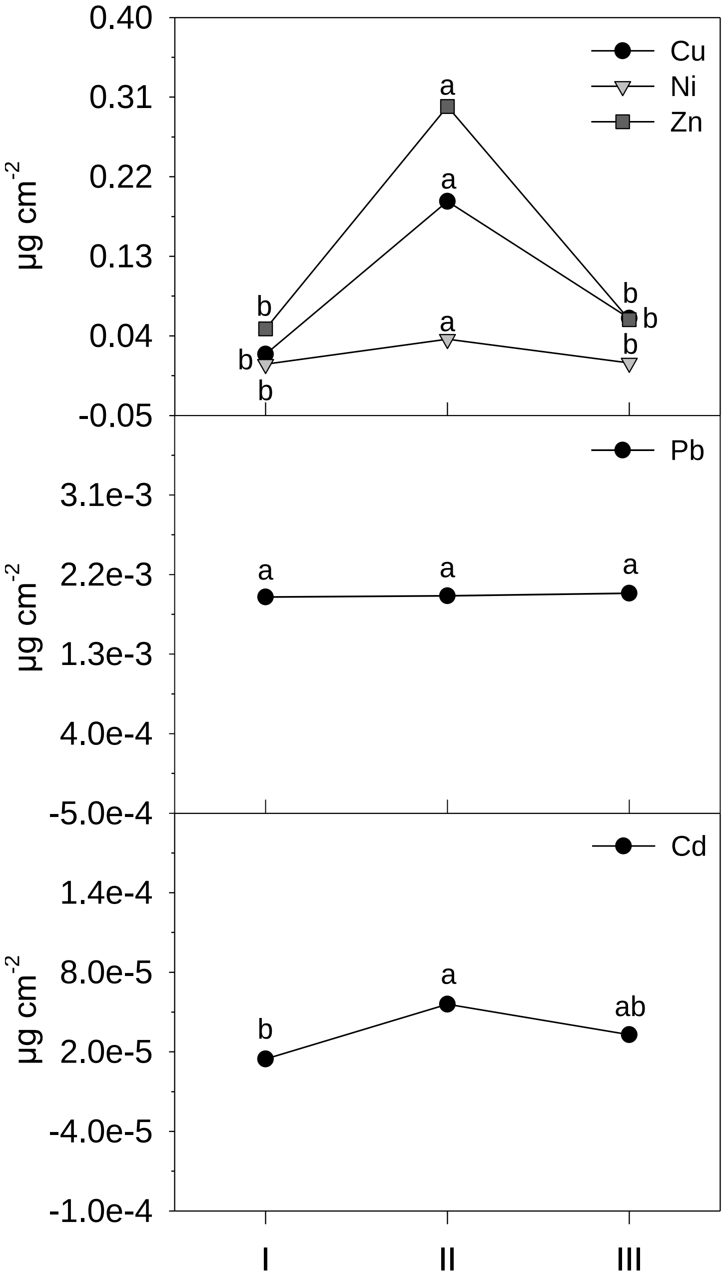


Figure 5: Elements accumulation on the leaf surface in the different periods: 21/06/2011 (I); 03/08/2011 (II); 04/10/2011 (III); 30/08. Values are means over all species (μg $cm^{-2}$).

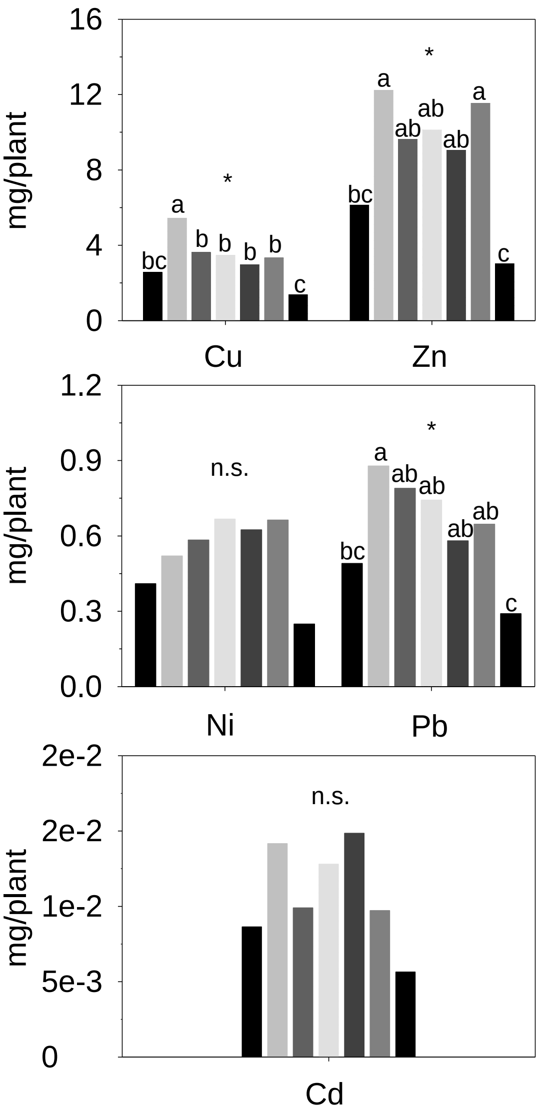


Figure 6: Element accumulation (from June to October 2011), in the water collected at the base of *Viburnum lucidum*, *Arbutus unedo*, *Photinia x fraseri*, *Laurus nobilis*, *Elaeagnus x ebbingei*, *Ligustrum japonicum* and Control water. Samples in graphics are reported in the same aforementioned order with different tones of grey. Values are means (mg/plant) ± SD. Significant differences among species are indicated at P<0.05 (*) using Duncan's MRT.

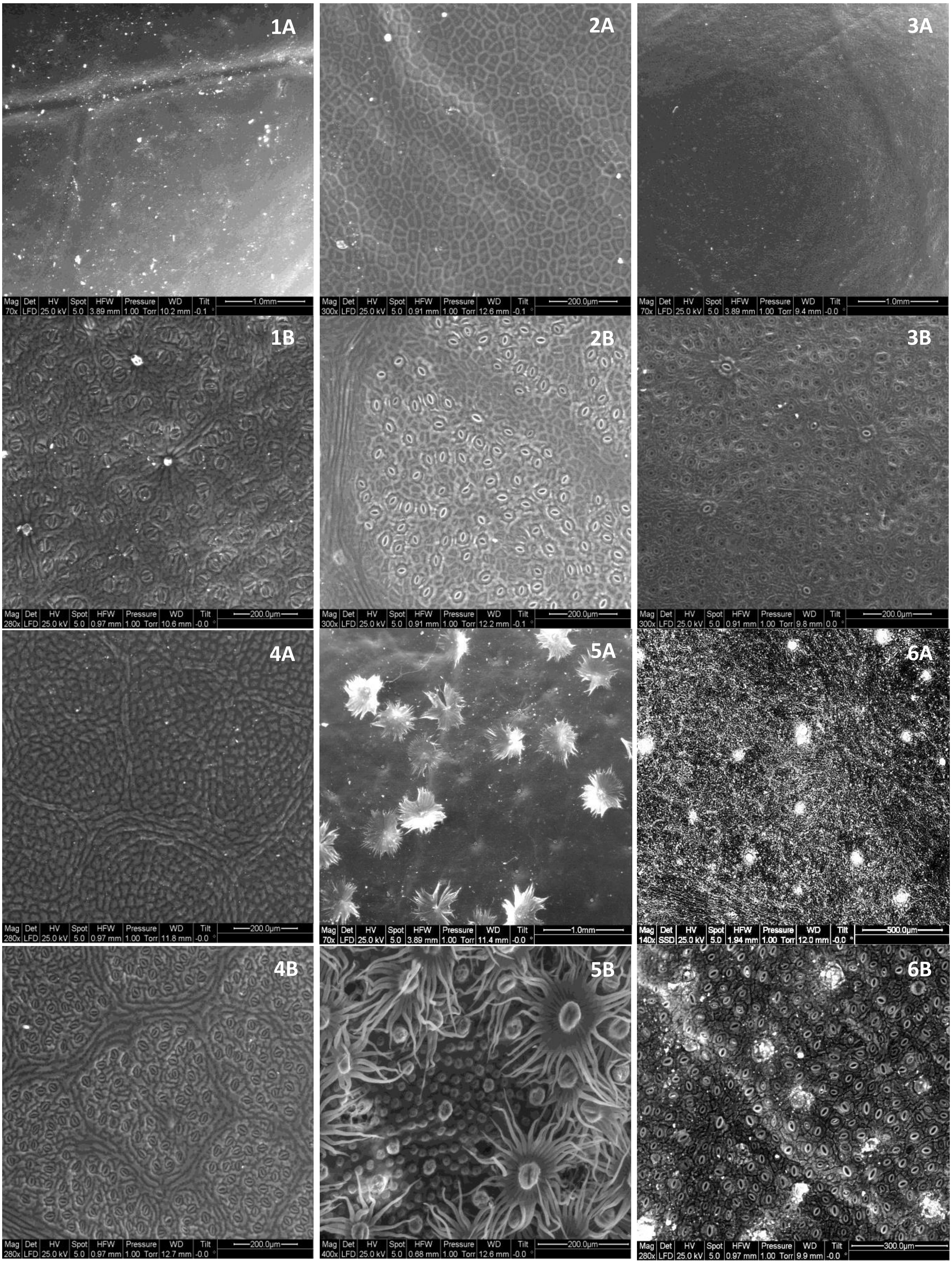
1A
2A
3A
1B
2B
3B
4A
5A
6A
4B
5B
6B

Figure 7: SEM micrographies of adaxial (A) and abaxial leaf surface (B) of *Viburnum lucidum* (1), *Arbutus unedo* (2), *Photinia x fraseri* (3), *Laurus nobilis* (4), *Elaeagnus x ebbingei* (5) and *Ligustrum japonicum* (6). Images were taken at different magnifications as reported on the images.

Table 1. Leaf area ($m^2$) of the six shrub species at planting date, used for trace metals analysis.

| Species | Mean | SD |
|---|---|---|
| *V.lucidum* | 0.41 | 0.04 |
| *A.unedo* | 0.30 | 001 |
| *P.x fraseri* | 0.35 | 0.05 |
| *L.nobilis* | 0.44 | 0.09 |
| *E.x ebbingei* | 0.50 | 0.06 |
| *L.japonicum* | 0.20 | 0.05 |

Table 2: Foliar deposition per unit leaf area or on the whole canopy of six shrub species of five trace metals (Cd, Cu, Ni, Pb and Zn). Data are the average of three samplings performed in June, August and October. Data are means ± SD. ANOVA tests of differences between species are also included. Values as 0.000 are minor than 0.001.

| Accumulation per unit leaf area (µg $cm^{-2}$ *1000) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *V. lucidum* | | *A.unedo* | | *P. x fraseri* | | *L. nobilis* | | *E. x ebbingei* | | *L. japonicum* | | | |
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | *F* | *P* |
| Cd | 0.048 | 0.059 | 0.037 | 0.053 | 0.026 | 0.040 | 0.036 | 0.059 | 0.025 | 0.052 | 0.031 | 0.053 | 0.31 | 0.899 |
| Cu | 81.36 | 83.74 | 96.35 | 109.0 | 70.05 | 65.61 | 116.0 | 158.2 | 107.5 | 123.2 | 69.60 | 56.18 | 0.83 | 0.545 |
| Ni | 14.83 | 17.73 | 17.05 | 17.51 | 11.78 | 13.12 | 25.14 | 31.68 | 24.43 | 26.62 | 18.04 | 14.94 | 1.02 | 0.440 |
| Pb | 2.373 | 1.352 | 1.617 | 1.249 | 1.890 | 0.960 | 1.251 | 1.034 | 2.092 | 0.721 | 2.546 | 0.752 | 3.71 | 0.022 |
| Zn | 92.28 | 82.35 | 140.4 | 131.1 | 114.2 | 126.5 | 182.3 | 201.4 | 164.0 | 155.1 | 145.8 | 132.9 | 2.33 | 0.090 |
| Accumulation on the whole plant (mg) | | | | | | | | | | | | | | |
| | *V. lucidum* | | *A.unedo* | | *P. x fraseri* | | *L. nobilis* | | *E. x ebbingei* | | *L. japonicum* | | | |
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | *F* | *P* |
| Cd | 0.002 | 0.003 | 0.001 | 0.002 | 0.001 | 0.002 | 0.001 | 0.002 | 0.002 | 0.005 | 0.001 | 0.002 | 0.44 | 0.816 |
| Cu | 4.076 | 4.195 | 3.841 | 4.345 | 3.907 | 3.660 | 3.064 | 4.477 | 10.14 | 11.62 | 2.450 | 2.218 | 2.46 | 0.043 |
| Ni | 0.743 | 0.888 | 0.680 | 0.698 | 0.657 | 0.732 | 0.730 | 0.920 | 2.304 | 2.511 | 0.572 | 0.589 | 3.16 | 0.014 |
| Pb | 0.108 | 0.074 | 0.064 | 0.050 | 0.105 | 0.054 | 0.033 | 0.031 | 0.161 | 0.100 | 0.099 | 0.029 | 5.53 | 0.000 |
| Zn | 4.623 | 4.126 | 5.597 | 5.228 | 6.371 | 7.058 | 5.296 | 5.851 | 15.45 | 14.63 | 5.130 | 5.168 | 3.08 | 0.015 |

Table 3: Partial least square regression analysis (PLSR) coefficients showing how accumulation of the different elements depends on wind velocity (Wind), air temperature (Air T°), relative humidity (RH%), and precipitation (Prec.). Values as 0.000 are not equal to 0 but minor than 0.001.

| | *F* | *P* | $r^2$ | Const. | Wind | Air T° | RH% | Prec. |
|---|---|---|---|---|---|---|---|---|
| Cd | 10.74 | 0.002 | 15 | -0.000 | 0.000 | 0.000 | -0.000 | -0.000 |
| Cu | 34.41 | 0.000 | 53 | -0.732 | 0.486 | 0.048 | -0.009 | -0.001 |
| Ni | 19.98 | 0.000 | 40 | -0.121 | 0.086 | 0.007 | -0.001 | -0.000 |
| Pb | 3.24 | 0.077 | 5 | -0.001 | 0.002 | 0.000 | -0.000 | -0.000 |
| Zn | 128.18 | 0.000 | 67 | -1.159 | 0.801 | 0.071 | -0.012 | -0.002 |

Table 4: Cluster derived from Cluster analysis and Factor loadings of two factors identified in the Factor analysis for the element on leaves during the whole sampling period. Varimax rotation was applied to factor analysis.

| | Cluster | Factor 1 | Factor 2 |
|---|---|---|---|
| Cd | 2 | 0.25 | **0.83** |
| Cu | 1 | **0.97** | 0.09 |
| Ni | 1 | **0.96** | 0.01 |
| Pb | 2 | -0.02 | **0.89** |
| Zn | 2 | **0.88** | 0.28 |

Table 5: Leaf area of the whole plant (LA), leaf area index (LAI), average lamina size (LS), number of leaves per plant (N°L), crown diameter (CD) and height of plants (HP), in six shrub species planted in the field near a heavily polluted road. Values are means ± SD. ANOVA tests of differences between species are also included.

| | *V.lucidum* | | *A.unedo* | | *P.x fraseri* | | *L.nobilis* | | *E.x ebbingei* | | *L.japonicum* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | *F* | *P* |
| LA ($m^2$) | 5.01 | 0.67 | 3.99 | 0.39 | 5.58 | 1.58 | 2.9 | 0.24 | 9.43 | 0.68 | 3.87 | 0.56 | 24.33 | 0.000 |
| LAI | 5.43 | 1.12 | 3.9 | 0.97 | 5.32 | 0.88 | 4.47 | 1.26 | 6.9 | 1.14 | 4.15 | 1.08 | 17.64 | 0.000 |
| LS($cm^2$) | 31.9 | 5.66 | 10.5 | 2.68 | 19.5 | 1.45 | 20.8 | 4.17 | 12.6 | 1.49 | 17.3 | 2.04 | 31.60 | 0.000 |
| N° L | 1608 | 265 | 3967 | 898 | 2876 | 226 | 1443 | 271 | 7611 | 1045 | 2268 | 284 | 88.06 | 0.000 |
| CD | 102 | 7.06 | 93.1 | 6.45 | 102 | 13.2 | 71.6 | 12.2 | 108 | 11.7 | 81.5 | 14.4 | 25.15 | 0.000 |
| HP | 146 | 16.8 | 136 | 11.5 | 194 | 28.7 | 166 | 9.99 | 170 | 31.8 | 162 | 24.9 | 13.44 | 0.000 |

## Paper II

Submitted to Urban Forestry & Urban Greening.

# Accumulation of traffic related air pollutants on leaves of six evergreen shrub species during Mediterranean summer season

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**Abstract**

Six evergreen shrub species (*Viburnum tinus subsp. lucidum* L., *Arbutus unedo* L., *Photinia x fraseri* Dress., *Laurus nobilis* L., *Elaeagnus x ebbingei* L., *Ligustrum japonicum* Thunb.) were tested for their capacity to accumulate pollutants on their current season leaves in Mediterranean environment. Plants were planted along a road in 2010 and exposed to traffic pollution. Leaf element deposition (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn) was analysed six times from early summer to early autumn 2012. Particulate matter on leaves, element concentration of particulate matter in the air and meteorological parameters were measured. Elements on leaves were related to meteorological conditions to study the inter-relations. *E. x ebbingei*, *P. x fraseri* and *V. lucidum* were found to accumulate most pollutants, *L. nobilis* and *A. unedo* were the lowest accumulators. A clear common trend of element accumulations was found.

Generally, elements increased from the first to the second sampling (28/6-19/7) and, thereafter, decreased until the early autumn. Element depositions depended on species and meteorological parameters. High growth rate (leaf surface, LAI, crown diameter, height of plants), seems to increase the relative pollutant retention capacity of plants. Rain decreased the element accumulation on leaves whilst increase in wind velocity and elements concentrations (in the air), tended to increase the presence of elements on leaves. Meteorological conditions were confirmed to be important factors modifying the dynamics of pollution deposition and their removal from leaves during a season.

Key words: EF, Element leaf depositions, growth parameters, meteorological parameters, particulate matter, seasonal trend.

**Introduction**

Air pollution poses significant threats to health worldwide and more than 2 million premature deaths each year can be attributed to the effects of urban air pollution (WHO, 2005). Danielis and Chiabai (1998) estimated that 5096 inhabitants in cities of Italy, would die because of exposure to transport-related pollution in 1993. Particulate matter (PM) is the principal non-gaseous component of air pollutants, comprising a mixture of elements, heavy metals, black carbon, polycyclic aromatic hydrocarbons and other substances suspended in the atmosphere (Bell et al., 2011). PM is defined as coarse (2.5– 10 μm), fine (0.1–2.5 μm), and ultrafine (≤0.1 μm) according to the diameter of the particles (Beckett et al., 1998). PM derives mainly from anthropogenic activities, with the transport related activities and industrial processes as the main sources (Suzuki, 2006; Sawidis et al., 2011). PM emissions from road vehicles include exhaust emissions and emissions due to wear (non-exhaust emissions). Non-exhaust emissions contribute mainly to the coarse fraction of PM, while exhaust emissions contribute predominantly to fine PM (Abu-Allaban et al., 2002; Tervahattu et al., 2006; Thorpe et al., 2007; Kam et al., 2012), which are most damaging to health. Elevated levels of heavy metals (HM) are common in urban areas as results of both a wide range of human activities and natural processes (Lu et al., 2010). HM are strongly associated with PM (Duzgoren-Aydin et al., 2006). Plants surfaces have been suggested to be used for the capture of PM as means to improve air quality. Plant leaves cause adsorption and, in smaller quantities, absorption of particulate and gaseous pollutants (Nowak et al., 2000; Bealey et al., 2007). Several studies have evaluated different plant species for their capacity in capturing air pollutants (Dzierzanowski et al., 2011; Sawidis et al., 2011; Sæbø et al., 2012). A negative gradient of PM in the air from the outside towards the inner parts of an urban forest was found in the city of Christchurch, New Zealand (Cavanagh et al., 2009). Also in London a negative gradient of element concentrations was found on leaves of *Acer campestre* L., *Betula pubescens* L., *Chamaecyparis lawsonia* (A. Murray) and *Urtica dioica* L., at increasing distances from two heavily trafficked roads (Peachey et al., 2009). Seasonal accumulation (in May and in September), was found for Cr, Fe, Ni, Zn, Pb in leaves of *Aesculus hippocastanum* and *Tilia* spp (Aničić et al., 2011). However, we haven't found published evidences about the trend of pollution deposition during a season and related to weather conditions in a dry and warm area, as the Mediterranean basin. In the present study, we focus on evergreen shrubs, commonly used in urban green areas of southern Europe. Evergreen plants are able to intercept high quantities of air pollutants also during the winter season (Freer-Smith et al., 2005), when concentration of pollutants in the air is highest (Pikridas et al., 2013). Little focus on evergreen shrub species is a surprise, since evergreen coniferous species of trees have been shown to be very efficient in capturing PM. In addition, the space often is not sufficient for tree planting along streets and the presence of trees can also worsen the concentration of pollutants by the reduction of wind speed in street canyons (Buccolieri et al., 2009; Salmond et al., 2013). In the present work we compared six evergreen shrub species (*Viburnum tinus subsp. lucidum* L. thereafter reported as *V. lucidum*, *Arbutus unedo* L., *Photinia x fraseri* Dress., *Laurus nobilis* L., *Elaeagnus x ebbingei* L., *Ligustrum japonicum* Thunb.) for their capacity in accumulating elements on leaf surface from the early summer to the early autumn season. The aims of the present work were: 1) to quantify the capacity of six widely used shrub species to intercept particulate matter and elements on leaf surface; 2) to study the trend of pollutants on leaves, in external conditions, from early summer to early autumn season; 3) to relate pollution deposition with atmospheric parameters; 4) To find evidences which demonstrate the influence of traffic on the presence of elements on leaves and the contribution of other sources.

**Methods**

*Study area and plant material*

In March 2010, 50 three years old plants of six evergreen shrubs (*Viburnum lucidum*, *Arbutus unedo*, *Photinia x fraseri*, *Laurus nobilis*, *Elaeagnus x ebbingei*, *Ligustrum japonicum*), were planted along a 4-lanes road (N 43° 52' 57.7992", E 10° 40' 58.0692") in Pescia (Tuscany, Italy). Plants were planted parallel to the road to form 2 vegetation belts 30 m long and 5 m wide each, starting 1.5 m away from the road. Twenty-five plants per species, per belt, formed a 5 by 5 m section of the belt. At planting, plants were cut back to a height of 150 cm, with the exception of *L. japonicum* and *E. x ebbingei* which were 130 cm tall. Three plants per species were chosen to measure the initial total leaf area using a RS 2 XA illumination and camera system Haiser, Germany) and A3 Lightbox G.C.L., UK) with WinDIAS software (Dynamax Inc., USA) (Table 1). Plants were not fertilized and only irrigated during prolonged dry periods. Height of plants, crown diameter and leaf area index (LAI), were measured on 6 plants per species in three sampling events during summer 2012. LAI was measured by a ceptometer (AccuPAR LP-80, Decagon devices, inc., WA, USA), at one meter above the ground. In October 2012, three plants per species were harvested for biomass determination. Branches and leaves where oven-dried at 60°C until constant weight. Before drying, total leaf area of every harvested plants was measured. Observations of the morphology of the leaf surface and presence of PM on the abaxial and adaxial side were carried out using a Quanta 200, Environmental Scan Electronic Microscope (ESEM), FEI, with 70–300 times enlargement. Only current season and full expanded leaves were considered. Meteorological parameters (rain, wind speed and air-temperature), were measured at 1.5 meters height, from 28/06/2012 to 08/10/2012 by a meteorological station iMetos® SD (Pessl instruments, Weiz, Austria) placed within the experiment plot.

*Element content in PM deposited on air filtration filters*

Particulate matter in the air was collected using two dust meters (Maspres Meccaniche, Italy). The instrument had a constant air flow of 0.5 $m^3 h^{-1}$ and was equipped with PTFE membrane 1.2 µm 90 mm (Sartorius Stedim Biotech GmbH, Germany). The filters were analysed for elements contained in the deposited PM. Measure of element composition of air PM were started when the first leaf samples were collected. Depositions on PTFE membranes were digested using a Heating digester DK 6, (Velp® Scientifica, Usmate, Italy). Temperature of digestion was 110°C for 60 minutes. A mixture of 12 ml $HNO_3$ (65%) and $H_2O_2$ (30%) (10:2) v/v were added. Water cooling was applied at the heating digester in order to minimize loss of elements by evaporation. Finally the volume was adjusted to 25 ml with distilled water. Content of 21 elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn), was analysed at Buzzi Laboratories, Prato (Italy, ISO 17025 certified), by 7500 Series, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Agilent (USA). Filter blanks were digested and analysed like the other samples.

*Soil element content*

Ten samples of top-soil (200 g each) were collected in the study area at a depth 0 to 10 cm, from surfaces free from shrubs and tree vegetation (Skrbìc et al., 2012). Samples were dried at room temperature until a constant weight. Aggregates of the soil were ground, and sieved in order to eliminate particles larger than 2 mm. To obtain composite representative samples (control soil), 50 g of each sub sample of soil were combined. Three parallel samples of 0.5 g from the composite sample were analysed. Digestion was performed applying 24 ml of the acid mixture at 110°C for 60 minutes. Then, another 24 ml of the same acid mixture were added and a second cycle of digestion was initiated. The remaining details were the same of Air PM element composition analysis. The solutions were filtered through an ashless filter papers, pore size 8 µm (WhatmanTM, US), and then the volume was adjusted to 100 ml using distilled water. The same procedure was applied for blank samples.

*Sampling of leaves for PM and element analysis*

From June 2012 leaves were sampled six times, (28/06; 19/07; 09/08; 30/08; 18/09; 08/10), in order to study the seasonal trend. Only leaves formed in the current season were collected. Every sampling was made at least seven days after the last precipitation. Leaf samples (300 g) were collected separately for each of the species, from the two vegetation belts, including leaves from the ground level to the top of the plants. Leaves of each species were collected from vegetation at least 1.5 meters distant from the adjacent species in order to reduce the influence of the position. Leaves with pests or diseases were avoided. During the experiment, 72 samples were collected. Another 300 g of leaves were collected in the same way, for the analysis of internal element leaf content of every species. Four leaves per species were separately collected at every leaf sampling, for the analysis of PM on leaves.

*PM accumulation on leaves*

Approximately 1 $cm^2$ was cut off each collected leaf and studied through an optical confocal microscope (Axioskop 40, Zeiss, Germany), with 10x zoom. Images were made with a camera (Axiocam MR 5, Zeiss) using the Axiovision Rel.4.6 software (Zeiss). Percentage of leaf area covered with PM was measured by ImageJ software (Open source).

*Element accumulation on leaves*

To estimate the deposition of elements, leaves were analysed separately both with and without washing. Leaves collected for internal element composition were washed for 30 minutes in a solution of HCl 0,01 M (pH 2) with a stirrer at 60 rpm in order to suspend the material deposited on the leaf surfaces. The other leaf samples, representing the sum of element foliar tissue composition and element leaf deposition, were measured for the leaf area, dried at 70°C until constant weight and grounded using a TissueLyser II (Qiagen, USA). For all leaf samples 200 mg of ground plant tissue were digested following the same protocol already used for PTFE membrane. Surface deposition (µg $cm^{-2}$), was estimated by subtracting element content of foliar tissue (washed leaves) from element values of unwashed leaves. Total pollution accumulation per plant was calculated by multiplying the element depositions per unit surface and the mean total leaf area.

*Enrichment Factor*

The enrichment factor (EF) of elements on leaf samples was estimated (Lorenzini et al., 2006). We compared EF estimates using both the element composition of control soil (Skrbìc et al., 2012) and the average crustal element composition reported by Taylor and McLennan (1985). In the literature EF results were differently interpreted (Aničić et al., 2001; Serbula et al., 2012). In the present study, all elements not included in the lower homogeneous group (LSD test) were considered indicators of enrichment. In addition, to achieve an unequivocal result, only the elements enriched using both control soil and soil crust references were considered as "significantly enriched".

*Statistical analyses*

Differences in element accumulation among species, periods and their interactions (species x period), were tested with analysis of variance (ANOVA) with setting for repeated measures (CoStat 6.303, CoHort Software, Monterey, CA, USA). Elements which presented statistically significant interaction between species and periods were analysed separately from the other elements. The method used to discriminate among the means was the least significant difference (LSD). The outliers were identified with scatterplots and removed from the dataset. Thus, twenty-four outliers of 1512 values were removed from the dataset of elements. The relationships between element accumulation on leaves and climate parameters and concentration of elements in PM in the air was tested using Partial Least Square Regression (PLSR) for each separate (Rosipal and Trejo, 2001). The linear relationships between the accumulated elements were tested using Pearson product-moment correlation coefficients. Correlations between element accumulation and total deposited

PM on leaves were also tested. Analysis of variance (One-way Anova) was carried out on the two datasets of EF separately. Multivariate methods were used to identify possible sources of the different elements in addition to the traffic. Cluster Analysis (CA), was performed using the Ward method and Euclidean distance as metric. Factor Analysis (FA) with Varimax rotation was also applied.

**Results**

*Air quality at the site and soil contamination*

In the filters, Ca, Zn and Pb were found to be in high concentrations as compared to that observed in the soil (Table 2). On the other hand, soil had a higher content of Al, Cr and Ba, compared to the filters.

*Analysis of PM deposition on leaves*

*E. x ebbingei* was the most efficient accumulator with 0.60 % of the leaf area covered by PM, *L. nobilis,* with 0.27 % leaf cover represented the lowest value (Fig. 1). The percentage of the leaves covered with particles generally decreased significantly from the first sampling (early summer) to the later ones (early autumn). The species presented a different trend of accumulation during the periods (species x period), ($p=0.014$). Total leaf PM was positively correlated with both temperature and wind speed ($r= 0.29; 0.38$). In contrast, negative correlations were found between PM deposited and rain ( $r= -0.50$).

*Element accumulation on leaves*

The order of deposition of elements was Ca, K, Mg, Fe, Al, Mn, Ba, Zn, Cu, Ni, Cr, Pb, Se, V, Cd, Li, Mo, Sb, Co, As, Tl. Species differed in the deposition of 13 out of the 21 analysed elements over all sampling periods. All the elements changed with high significance ($P<0.001$) with the exception of Ba, Tl and Zn ($P<0.01$). *L. nobilis* and *A. unedo* had the smallest accumulation of elements per unit surface and were considered to be the least efficient accumulators. *E.* x *ebbingei*, *V. lucidum* and *P.* x *fraseri* accumulated the highest quantity of a large number of the elements analysed for, with the highest values for As, Cr and Fe (Table 3). Generally, the deposition of elements presented the same trend in the different species increasing form the first to the second period (28/06-19/07) and, thereafter, decreasing progressively until the last period (8/10), reaching to the initial levels (Fig. 2). However Cd, Cr, Cu, K, Li and Mn presented a statistically different trend depending on species (interaction Species x Period) (Fig. 3). Also in these elements an increase in the early summer and then a decrease until October was observed. Generally elements on leaves decreased after precipitation and increased with increase in element concentration in Air PM and at increase of wind speed (Table 4). A clear relationship between Air temperature and RH% on the accumulation of elements was not found. The model of Partial Least Square Regression was significant for all the elements with the exception of Ba, Mn, and Tl. In nine cases, the determination coefficient ($r^2$) exceeded the value of 0.5, and in Cr, Cu, Li and Se exceeded the value of 0.7. The species differed in the total accumulation of all the elements with the exception of Li and Sb (Table 5). *E. x ebbingei* with *V. lucidum and P. x fraseri* had also the highest values of accumulation per plant due to their highest leaf areas.

*Enrichment Factor (EF)*

Ca, K, Sb and Zn were found to be enriched in both datasets suggesting that their presence is due to a different source than the soil contribution by soil dust (Table 7). By the analysis all the other elements were found to be not significantly enriched.

*5 Element source identification using multivariate methods*

Two principal clusters of elements and three factors were found (Table 8). In the first cluster (CA), all the elements with the exception of As, Fe, and Zn were included. In FA, 78% of the variance may be explained by the first three factors. Factor 1, which accounted the 48.7% of the total variance, showed positive loadings with Cr, Cu, Li, Pb, Sb, Se and V. In factor 2 (17,4 % of variance), the dominant elements were As, Fe, K, Mn, Mo, Tl and Zn. Factor 3 (12.5% of variance) presented positive loadings with Al, Ba, Ca, Cd, Co, Mg, K and Ni. Correlation analysis highlighted eleven strong correlations (r>0.70). Fe was highly correlated with As (r=0.80), Ca with Mg and Ni (r=0.72), Cr with Cu, Li, and Se (r=0.73; 0.84; 0.70), Cu with Li, Pb, Se (r=0.79; 0.81; 0.86), K with Mg (r=0.74), Li with Se (r=0.77) (data not shown).

**Discussion**

*Air quality and soil contamination at the site*

The results of element concentrations of PM in filters (Table 2) agree with that reported in the literature (Bosco et al., 2005), indicating that the composition of PM was strongly affected by traffic emissions. In addition, soil and PM in filters presented a different element composition, suggesting that the soil is not the only contributor to the presence of elements in the air. Concentrations of Cd, Co, Cr, Cu, Ni, Pb, Se, Tl, V, Zn in soil (Table 2), exceeded the Italian limit values (D.Lgs 152/2006) for the residential and public areas. These results indicated that the traffic emissions enriched the concentration of some elements in the neighbouring soil and probably also on leaves surface.

*Element and PM accumulation on leaves*

In our work, the amount of pollutants on leaves were found to be conform to those obtained in a very polluted Mediterranean city (Bosco et al., 2005), and in a temperate one (Simon et al., 2011). These similarities indicate a significant contribution of traffic in the element accumulations on leaves. Species showed a different elements accumulation capacity. Total leaf area appears more important than accumulation per unit leaf area in setting total plant accumulation. In addition the combination of high growth parameters influences more the element depositions per unit leaf area than the morphology of leaf surface. *E.* x *ebbingei*, *V. lucidum* and *P. x fraseri*, which we found to accumulate most elements per unit leaf area and per plant, also had the highest values of Total leaf area, LAI and crown diameter (data not shown). On the other hand, *L. nobilis* and *A. unedo,* which we classified as low accumulators, also had low values of LAI and Leaf area. By the observations of the leaf surface carried out at SEM (data not shown), it was not possible to identify clear morphological characteristics which could explain the results of leaf accumulation. In fact *E.* x *ebbingei* presented an high presence of trichomes while *V. lucidum* and *P. x fraseri* are smooth. These results are unexpected considering that leaves with rough surfaces, was shown to be more effective in capturing pollution than those with smooth surfaces (Beckett et al. 2000). A more specific analysis of the leaf morphology could help the interpretation of results. Trees have an higher efficiency in capturing PM compare to the shorted vegetation (Fowler et al., 2003), due to their large total leaf areas that create more turbulent mixing of the air passing over the plants than observed at shorter vegetation (Beckett et al., 2000). The higher accumulation capacity of trees was also linked to their higher LAI (Bunzl et al., 1989). On the other hand, trees can also cause an increase of the concentration of pollution at the pedestrian level when planted in street canyons, by the reduction of the air circulation (Salmond et al., 2013). If high accumulation rates of pollutants on leaves surface is important when choosing species for urban greening or as an ecosystem service, *E x ebbingei, V. lucidum* and *P.x fraseri* represents a good choice. The accumulation on leaves changed significantly from early summer to early autumn in almost all elements and partially differed between species (Fig. 2 and 3). These results agree with that reported in the literature (Nowak et al., 2006) about the temporary retention of PM on leaves, and then of all the components therein. The results of PLS regression analysis (Table 4), with the high number of significant results (18 of 21), suggest that presence of the elements on leaves are negatively related to precipitation and positively related to wind velocity and element concentration in air. In the cases of Cr, Cu, Li the statistical model showed a high $r^2$ values. Thus, it may be possible to predict the accumulation of elements, by using the climate parameters and concentration of elements in air. This could be important input to modelling. The negative relation between depositions and rain confirms that rain removes depositions from plant leaves (Nowak et al., 2006). The capacity in increasing the element depositions of increasing wind speed was also confirmed (Beckett et al., 2000). The positive relation between the concentration of elements in the air PM and elements on leaves is explainable assuming that PM is the vector of the elements (Bell et al., 2011). Relative humidity and Air temperature were not found to have a clear influence on element depositions even if different evidences were published (Fowler et al., 2003; Litschke and Kuttler, 2008; Cavanagh et al., 2009). Ca, K, Sb and Zn were enriched on the leaf surfaces and, thus, probably originating from a different source than that of soil dust. Sb and Zn are typically associated with particulate pollution originating from traffic (Monaci et al., 2000; Peachey et al., 2009). Ca and K have been identified as products of tire wear (Apeagyei et al., 2011), but also as result of soil contribution (Zhao et al., 2006). Selenium presented a very different result of enrichment, depending on the used reference material, underlining the importance of the comparison chosen. The trend of total PM on leaves (Fig. 1), during the six periods has some common characteristics with the trend of the elements on leaves. In fact positive correlations were found between PM and ten elements. The correlation analysis between PM on leaves and the meteorological parameters confirmed the pattern of relationship already found for elements (data not shown).

*Element source identification using multivariate methods*

Different multivariate methods were compared in order to examine results according to possible sources of the different elements. As, Fe and Zn are clustered together in the CA and have high loadings in factor 2 of FA (Table 8). In addition As and Fe are highly correlated (r=0.80), but other high correlations were not found for these elements. High correlations were not found for Zn but it is interesting that the highest correlations are with As and Fe (r= 0.53 and 0.57, respectively). The relationships among As, Fe and Zn are then supported by three different multivariate methods. Ca is highly correlated with Mg and Ni (r=0.72 each) and these three elements are dominant in factor 3 of FA. Moreover, in CA they are clustered in the first group. Mg is highly correlated also with K (r=0.75). This relation is confirmed in CA and partially in FA, where K presents almost the same loadings in factor 2 and 3. Cr, Cu, Li, Se, and Pb presented a large number of high correlations. These elements are all present in cluster one of CA and all of them are dominants in factor 1 of FA.

Three different groups of elements were created considering only the elements which were supported in the three different multivariate methods: group 1 (Cr, Cu, Li, Se, Pb); group 2 (Ca, Mg, Ni and K); group 3 (As, Fe, Zn, K). Group 1 and 3 are both characterized by elements often related to traffic pollution and then was not easy to discriminate among them. A contribution from the agricultural activities can be conceivable for the group 1 given the presence of Cu which is largely used in the neighbouring area. Zinc is present in the products of tire wear and exhaust emissions (Allen et al., 2001). Fe, Cr and Cu also originate primarily from brake wear (Monaci et al., 2000). The presence of Zn, Cr, Pb and Cu was found in the exhaust emissions of oil combustion while As and Se derived from fuel combustion (Pulles et al., 2012). Group 2 is composed mainly by elements which are attributable to soil contribution. Ca, Mg and K are identified as crustal elements (Zhao et al., 2006), also due to their high presence in the composition of the upper crust (Taylor and McLennan, 1985). Potassium, which is present both group 1 and 2, can be attributable to traffic emission and probably also with substantial soil contributions. Almost all of the elements present in the three groups have been attributed directly or indirectly to the traffic emissions (Pant and Harrison, 2013). In contrast, some of these were also attributed to be indicators of the soil contribution (Monaci et al., 2000). The relations between elements are fundamental for the identification of the possible source. Also the numerous positive correlations between elements suggested that elements originate from a low number of sources (Monaci et al., 2000). The results of EF analysis and multivariate methods agree for what concerning Zn and partially for K. On the other hand disagree for Ca which resulted as soil contribution in the multivariate analysis and anthropogenic contribution in the EF analysis. The disagreement between these analysis highlights how more than one method can be used in order to better interpretate results. The accumulation of elements and PM seems to be linked to the growth parameters of plants. *E. x ebbingei*, *V. lucidum* and *P. x fraseri* were found to be the most suitable species in air pollution removal. The trend of pollutants from early summer to early autumn was detected for all the elements and was interpreted considering the meteorological parameters. Traffic was confirmed by different results to be the most influencing source of pollution in the considered area. Concluding the present work confirms, in open area, the role of species in pollution accumulation capacity and may provide useful information on widely spread species in urban areas of southern Europe.

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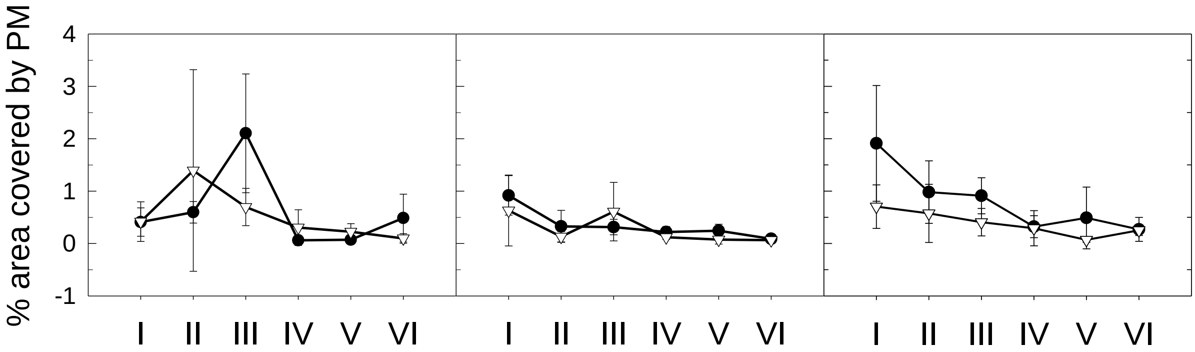
Fig. 1 Percent of the leaf covered with deposited particles in six shrub species analysed at 28/06/2012 (I); 19/07/2012 (II); 09/08/2012 (III); 30/08/2012 (IV); 18/09/2012 (V); 08/10/2012 (VI). Values are means (% area PM on leaf) ± SD. *V.lucidum*, *Photinia x fraseri* and *Elaeagnus x ebbingei* (dark circle), are indicated with the same consecutive order. *Arbutus unedo*, *Laurus nobilis* and *Ligustrum japonicum* (white triangle down), are indicated with the same consecutive order.



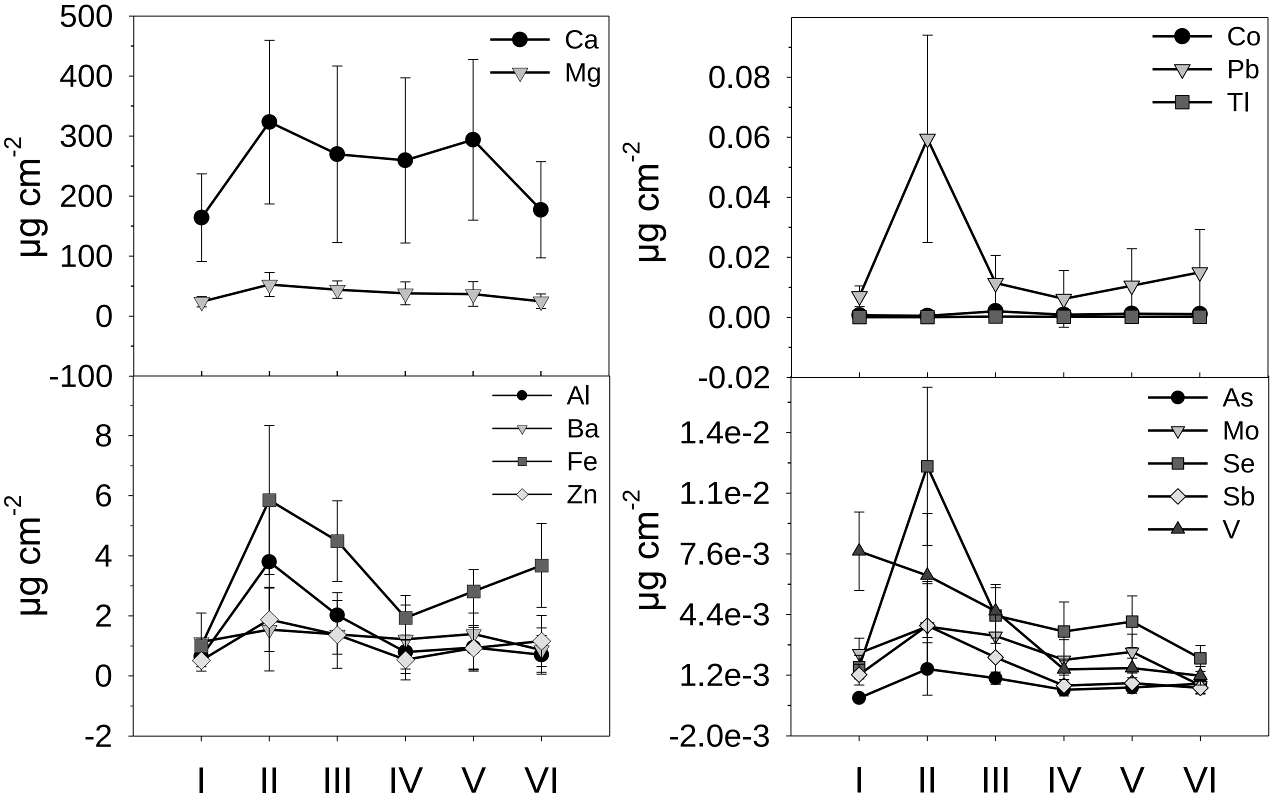



Fig. 2. Element leaf deposition in the different periods: 28/06/2012 (I); 19/07/2012 (II); 09/08/2012 (III); 30/08/2012 (IV); 18/09/2012 (V); 08/10/2012 (VI). Only elements which not presented an interaction between species and period are shown. Values are means over all species (µg $cm^{-2}$) ±
460 SD. Elements where a period by species interaction was found are presented in Fig. 3.

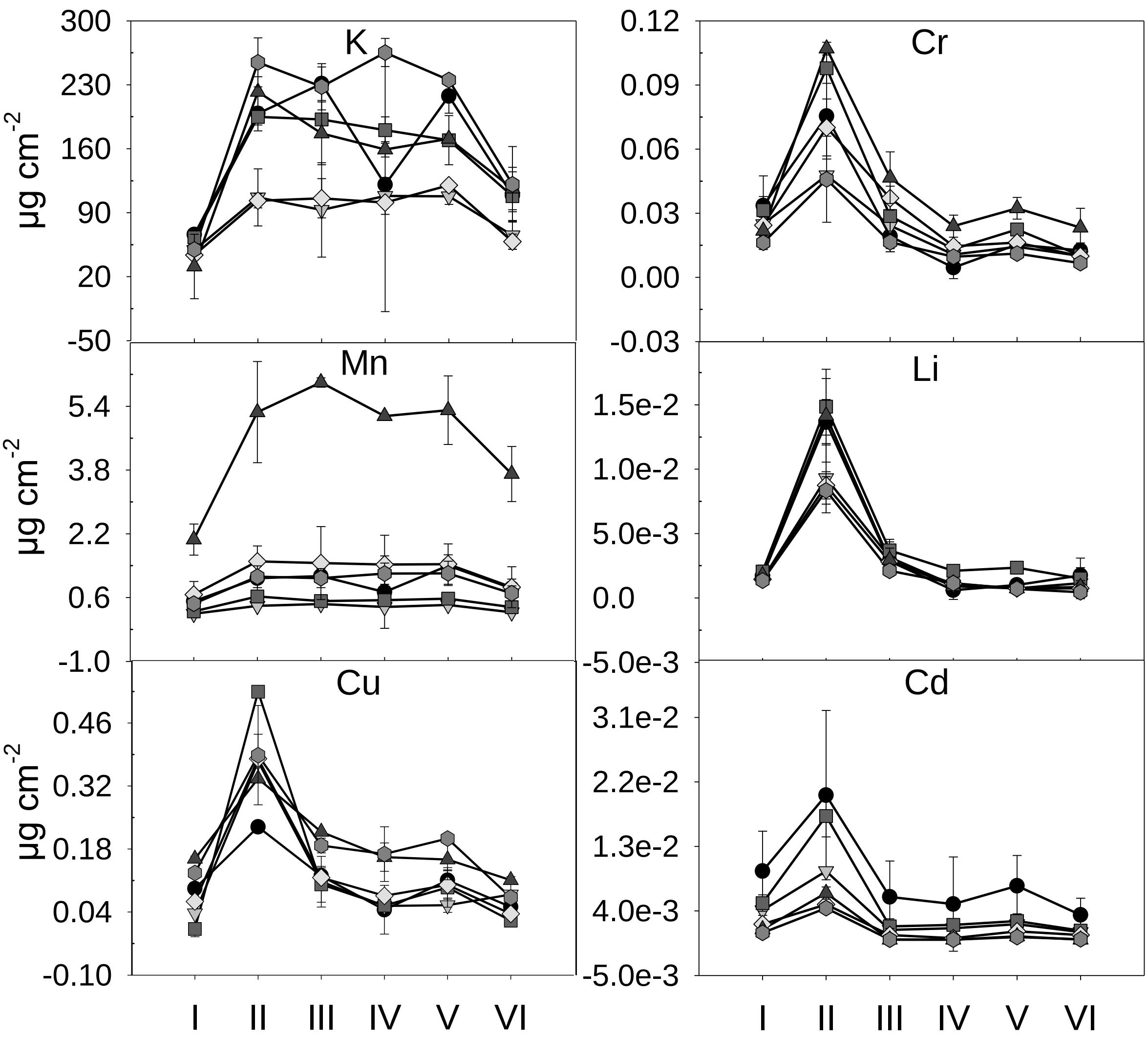



Fig. 3. Leaf deposition of different elements in *Viburnum lucidum* (black circle), *Arbutus unedo* (white triangle down), *Photinia x fraseri* (black square), *Laurus nobilis* (white diamond), *Elaeagnus x ebbingei* (black triangle up), and *Ligustrum japonicum* (white circle) are reported. Data are referred to different sampling periods: 28/06/2012 (I); 19/07/2012 (II); 09/08/2012 (III); 30/08/2012 (IV); 18/09/2012 (V); 08/10/2012 (VI). They are reported only the elements where an interaction between species and period was detected. Values are means (µg $cm^{-2}$) ± SD.

Table 1. Leaf area ($m^2$) per plant of the six shrub species at planting date.

| Species | Mean | SD |
|---|---|---|
| *V.lucidum* | 0,41 | 0,04 |
| *A.unedo* | 0,30 | 0,01 |
| *P.x fraseri* | 0,35 | 0,05 |
| *L.nobilis* | 0,44 | 0,09 |
| *E.x ebbingei* | 0,50 | 0,06 |
| *L.japonicum* | 0,20 | 0,05 |

Table 2. Element accumulation of air filtration filters during the whole sampling period (µg $filter^{-1}$) and element concentrations in soil (ppm) at the study site.

| | Filters | | Soil | |
|---|---|---|---|---|
| | Mean | SD | Mean | SD |
| Al | 69,30 | 97,29 | 78060 | 169,7 |
| As | 0,033 | 0,055 | 13,69 | 0,280 |
| Ba | 2,588 | 4,357 | 436,3 | 4,920 |
| Ca | 514,3 | 770,5 | 7719 | 190,5 |
| Cd | 0,036 | 0,054 | 2,060 | 0,080 |
| Co | 0,101 | 0,127 | 21,46 | 18,56 |
| Cr | 0,798 | 0,869 | 230,1 | 5,790 |
| Cu | 6,381 | 9,897 | 156,1 | 0,760 |
| Fe | 84,90 | 82,22 | 69967 | 257,2 |
| K | 56,42 | 67,09 | 10689 | 236,0 |
| Li | 0,137 | 0,227 | 121,5 | 0,740 |
| Mg | 84,25 | 127,8 | 34787 | 371,1 |
| Mn | 4,186 | 6,106 | 1884 | 21,46 |
| Mo | 0,227 | 0,360 | 0,760 | 0,100 |
| Ni | 0,638 | 0,588 | 154,0 | 1,840 |
| Pb | 3,240 | 3,458 | 129,7 | 3,040 |
| Sb | 0,204 | 0,249 | 0,060 | 0,030 |
| Se | 0,035 | 0,043 | 5,810 | 0,240 |
| Tl | 0,001 | 0,003 | 1,330 | 0,020 |
| V | 0,233 | 0,344 | 129,2 | 0,990 |
| Zn | 20,58 | 27,40 | 213,9 | 14,21 |

Table 3. Element leaf deposition in six shrub species during three months in the summer of 2012. Values are means (µg cm$^{-2}$) ± SD. ANOVA tests of differences between species are also included. Values as 0,000 are minor than 0,001.

| | *V.lucidum* | | *A.unedo* | | *P. x fraseri* | | *L. nobilis* | | *E. x ebbingei* | | *L. japonicum* | | Tests | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | *F* | *P* |
| Al | 3.044 | 2.240 | 1.283 | 1.224 | 1.366 | 1.493 | 1.000 | 0.732 | 1.553 | 1.674 | 0.865 | 0.618 | 3.60 | 0.093 |
| As | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.000 | 0.000 | 0.001 | 0.001 | 0.001 | 0.000 | 1.24 | 0.408 |
| Ba | 2.790 | 1.148 | 2.157 | 0.466 | 1.361 | 0.311 | 0.100 | 0.032 | 0.432 | 0.153 | 0.710 | 0.208 | 14.97 | 0.005 |
| Ca | 358.4 | 141.0 | 167.1 | 76.05 | 318.4 | 85.06 | 95.78 | 27.26 | 337.4 | 104.2 | 210.0 | 71.92 | 12.58 | 0.007 |
| Cd | 0.009 | 0.008 | 0.003 | 0.003 | 0.005 | 0.006 | 0.002 | 0.002 | 0.001 | 0.003 | 0.001 | 0.002 | 2.92 | 0.132 |
| Co | 0.002 | 0.001 | 0.001 | 0.005 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 14.85 | 0.005 |
| Cr | 0.027 | 0.025 | 0.020 | 0.013 | 0.036 | 0.034 | 0.029 | 0.022 | 0.043 | 0.032 | 0.018 | 0.015 | 13.06 | 0.007 |
| Cu | 0.102 | 0.063 | 0.118 | 0.125 | 0.098 | 0.156 | 0.130 | 0.122 | 0.184 | 0.071 | 0.190 | 0.120 | 7.29 | 0.024 |
| Fe | 3.338 | 2.615 | 2.936 | 1.598 | 3.799 | 2.088 | 2.414 | 1.174 | 4.611 | 2.811 | 2.674 | 1.157 | 4.38 | 0.065 |
| K | 157.2 | 77.63 | 88.44 | 31.36 | 159.3 | 48.99 | 88.68 | 29.78 | 146.1 | 65.08 | 192.3 | 84.63 | 10.77 | 0.010 |
| Li | 0.004 | 0.005 | 0.003 | 0.003 | 0.004 | 0.005 | 0.003 | 0.003 | 0.004 | 0.005 | 0.002 | 0.003 | 5.31 | 0.045 |
| Mg | 44.20 | 18.39 | 29.35 | 8.846 | 51.82 | 17.44 | 14.05 | 6.464 | 36.50 | 16.36 | 46.24 | 16.58 | 14.99 | 0.005 |
| Mn | 0.952 | 0.445 | 0.340 | 0.101 | 0.480 | 0.146 | 1.231 | 0.562 | 4.580 | 1.475 | 0.963 | 0.347 | 62.55 | 0.000 |
| Mo | 0.002 | 0.001 | 0.002 | 0.002 | 0.003 | 0.002 | 0.002 | 0.001 | 0.003 | 0.002 | 0.003 | 0.001 | 1.08 | 0.469 |
| Ni | 0.095 | 0.060 | 0.015 | 0.006 | 0.048 | 0.023 | 0.024 | 0.020 | 0.080 | 0.026 | 0.019 | 0.009 | 4.32 | 0.067 |
| Pb | 0.022 | 0.028 | 0.013 | 0.018 | 0.022 | 0.041 | 0.010 | 0.011 | 0.031 | 0.018 | 0.009 | 0.012 | 7.36 | 0.024 |
| Sb | 0.001 | 0.002 | 0.002 | 0.002 | 0.002 | 0.001 | 0.001 | 0.001 | 0.002 | 0.002 | 0.001 | 0.001 | 2.32 | 0.000 |
| Se | 0.005 | 0.005 | 0.004 | 0.002 | 0.005 | 0.005 | 0.003 | 0.004 | 0.006 | 0.005 | 0.005 | 0.004 | 5.12 | 0.049 |
| Tl | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.19 | 0.114 |
| V | 0.004 | 0.004 | 0.003 | 0.003 | 0.004 | 0.003 | 0.003 | 0.002 | 0.005 | 0.004 | 0.003 | 0.003 | 3.61 | 0.093 |
| Zn | 1.216 | 1.023 | 0.905 | 0.628 | 1.363 | 1.324 | 0.836 | 0.574 | 1.028 | 0.509 | 0.978 | 0.855 | 5.48 | 0.043 |

Table 4. Partial least square regression analysis showing how accumulation of the different elements is influenced by different factors as the elements concentration in Tot air PM (PM), wind velocity (Wind), air temperature (Air T°), relative humidity (RH%), and precipitation (Prec.).

| | *F* | *P* | $r^2$ | Const. | PM | Wind | Air T° | RH% | Prec. |
|---|---|---|---|---|---|---|---|---|---|
| Al | 22.5 | 0.00 | 51 | -11.1 | 0.02 | 8.93 | -0.03 | 0.13 | -0.01 |
| As | 5.45 | 0.01 | 20 | 0.00 | -0.09 | 0.00 | 0.00 | -0.00 | -0.00 |
| Ba | 1.17 | 0.32 | 5 | 1.98 | -0.22 | 1.57 | -0.01 | -0.02 | 0.00 |
| Ca | 4.38 | 0.02 | 16 | 350 | 0.73 | 170 | -4.96 | -3.15 | 0.74 |
| Cd | 22.2 | 0.00 | 50 | -0.00 | 0.05 | 0.01 | -0.00 | 0.00 | -0.00 |
| Co | 15.7 | 0.00 | 42 | 0.01 | -0.04 | -0.01 | 0.00 | -0.00 | -0.00 |
| Cr | 90.1 | 0.00 | 81 | -0.03 | 0.04 | 0.05 | -0.00 | 0.00 | -0.00 |
| Cu | 81.5 | 0.00 | 81 | -0.10 | 0.06 | 0.23 | -0.00 | -0.00 | -0.00 |
| Fe | 10.8 | 0.00 | 33 | -6.90 | 0.03 | 0.53 | 0.07 | 0.14 | -0.02 |
| K | 9.92 | 0.00 | 31 | 342 | 1.08 | 93.5 | -1.41 | -4.14 | 0.56 |
| Li | 98.4 | 0.00 | 82 | -0.05 | 0.34 | 0.02 | -0.00 | 0.00 | -0.00 |
| Mg | 8.09 | 0.00 | 27 | -9.79 | -0.03 | 74.8 | -0.11 | 0.09 | -0.01 |
| Mn | 0.55 | 0.58 | 2 | 2.78 | 0.29 | 0.46 | -0.01 | -0.03 | 0.00 |
| Mo | 14.4 | 0.00 | 40 | 0.00 | -0.00 | 0.00 | 0.00 | -0.00 | -0.00 |
| Ni | 3.96 | 0.03 | 15 | -0.05 | 0.03 | 0.04 | 0.00 | 0.00 | -0.00 |
| Pb | 23.5 | 0.00 | 53 | -0.07 | 0.02 | 0.03 | -0.00 | 0.00 | -0.00 |
| Sb | 22.7 | 0.00 | 51 | 0.00 | -0.01 | 0.00 | 0.00 | -0.00 | -0.00 |
| Se | 66.1 | 0.00 | 75 | -0.00 | 0.07 | 0.01 | 0.00 | -0.00 | -0.00 |
| Tl | 0.29 | 0.75 | 1 | 0.00 | 0.02 | -0.00 | 0.00 | -0.00 | 0.00 |
| V | 38.2 | 0.00 | 64 | -0.00 | -0.02 | 0.01 | 0.00 | -0.00 | -0.00 |
| Zn | 3.51 | 0.04 | 14 | -1.77 | 0.01 | 0.79 | 0.03 | 0.03 | -0.01 |

Table 5. Element accumulation on the whole plant in the different species during the whole sampling period. Values are mg plant$^{-1}$ ± SD. ANOVA tests of differences between species are also included.

| | *A. unedo* | | *E. x ebbingei* | | *L. japonicum* | | *L. nobilis* | | *P. x fraseri* | | *V. lucidum* | | Test | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Mean | SD | *F* | *P* |
| Al | 85.88 | 23.66 | 215.8 | 67.16 | 59.32 | 42.38 | 64.36 | 13.61 | 159.3 | 50.25 | 228.7 | 54.65 | 3.19 | 0.012 |
| As | 0.052 | 0.020 | 0.139 | 0.049 | 0.046 | 0.027 | 0.024 | 0.004 | 0.082 | 0.022 | 0.061 | 0.013 | 2.71 | 0.027 |
| Ba | 132.3 | 14.58 | 60.16 | 6.137 | 44.63 | 19.16 | 6.464 | 0.596 | 158.6 | 10.48 | 228.7 | 27.16 | 36.47 | 0.000 |
| Ca | 11186 | 1470 | 46884 | 4179 | 14397 | 4932 | 6167 | 506.8 | 37126 | 2863 | 29383 | 3336 | 37.81 | 0.000 |
| Cd | 0.221 | 0.061 | 0.195 | 0.099 | 0.066 | 0.113 | 0.104 | 0.032 | 0.585 | 0.200 | 0.704 | 0.179 | 4.85 | 0.001 |
| Co | 0.052 | 0.011 | 0.175 | 0.025 | 0.057 | 0.035 | 0.039 | 0.008 | 0.168 | 0.020 | 0.138 | 0.025 | 12.05 | 0.000 |
| Cr | 1.206 | 0.250 | 5.907 | 1.276 | 1.212 | 1.032 | 1.850 | 0.406 | 3.831 | 1.091 | 2.196 | 0.601 | 5.83 | 0.000 |
| Cu | 7.892 | 2.416 | 21.28 | 3.708 | 11.96 | 8.398 | 8.303 | 2.273 | 10.48 | 4.894 | 6.950 | 1.551 | 2.95 | 0.018 |
| Fe | 196.6 | 30.89 | 640.8 | 112.8 | 183.3 | 79.35 | 155.5 | 21.82 | 443.0 | 70.29 | 273.7 | 61.88 | 9.27 | 0.000 |
| K | 5921 | 606.1 | 20301 | 2611 | 13183 | 5803 | 5710 | 553.6 | 17023 | 2159 | 12886 | 1837 | 11.22 | 0.000 |
| Li | 0.187 | 0.064 | 0.495 | 0.206 | 0.162 | 0.197 | 0.167 | 0.056 | 0.516 | 0.167 | 0.294 | 0.114 | 1.72 | 0.143 |
| Mg | 1965 | 171.0 | 4649 | 733.1 | 3171 | 1136 | 904.5 | 120.1 | 5538 | 735.3 | 3624 | 435.3 | 12.24 | 0.000 |
| Mn | 22.75 | 1.947 | 636.4 | 59.17 | 66.05 | 23.80 | 79.26 | 10.44 | 55.99 | 4.920 | 78.05 | 10.52 | 88.07 | 0.000 |
| Mo | 0.097 | 0.031 | 0.402 | 0.084 | 0.228 | 0.089 | 0.150 | 0.019 | 0.311 | 0.056 | 0.130 | 0.031 | 6.40 | 0.000 |
| Ni | 1.005 | 0.124 | 11.09 | 1.025 | 1.281 | 0.605 | 1.563 | 0.374 | 5.623 | 0.766 | 7.098 | 1.501 | 24.31 | 0.000 |
| Pb | 0.893 | 0.354 | 3.964 | 0.765 | 0.622 | 0.842 | 0.632 | 0.211 | 2.582 | 1.379 | 1.799 | 0.663 | 3.37 | 0.009 |
| Sb | 0.104 | 0.034 | 0.275 | 0.094 | 0.094 | 0.082 | 0.074 | 0.020 | 0.183 | 0.047 | 0.118 | 0.041 | 2.29 | 0.056 |
| Se | 0.233 | 0.047 | 0.854 | 0.184 | 0.310 | 0.244 | 0.204 | 0.067 | 0.605 | 0.168 | 0.434 | 0.111 | 4.40 | 0.002 |
| Tl | 0.006 | 0.001 | 0.035 | 0.006 | 0.010 | 0.008 | 0.000 | 0.000 | 0.079 | 0.015 | 0.000 | 0.000 | 20.89 | 0.000 |
| V | 0.222 | 0.051 | 0.672 | 0.147 | 0.222 | 0.183 | 0.197 | 0.045 | 0.503 | 0.111 | 0.348 | 0.090 | 4.42 | 0.002 |
| Zn | 60.56 | 12.15 | 131.1 | 22.82 | 67.07 | 58.59 | 53.85 | 10.67 | 145.7 | 44.52 | 99.72 | 24.21 | 2.48 | 0.040 |

Table 7. Comparison of the EFs calculated with the elements composition of control soil and the average of the element composition of the upper crust as reference materials. H.G (Homogeneous group derived by the multi-comparison test of means tested by Least Square Difference test). The grey lines highlighted the elements which were enriched in both cases.

| EF | Average upper crust | | | Control soil | | |
|---|---|---|---|---|---|---|
| | Mean | SD | H.G | Mean | SD | H.G |
| Al | 1,000 | 0,000 | A | 1,000 | 0,000 | A |
| As | 26,77 | 19,04 | A | 4,920 | 5,070 | A |
| Ba | 170,1 | 164,4 | AB | 241,2 | 278,4 | BC |
| Ca | 733,1 | 570,9 | DE | 2641 | 1977 | F |
| Cd | 1713 | 1707 | F | 103,9 | 113,6 | ABC |
| Co | 9,980 | 7,910 | A | 4,850 | 3,480 | A |
| Cr | 58,46 | 32,87 | A | 21,32 | 107,8 | A |
| Cu | 486,5 | 411,7 | CD | 88,66 | 118,2 | ABC |
| Fe | 8,370 | 9,300 | A | 4,070 | 4,520 | A |
| K | 450,6 | 385,3 | BC | 1146 | 980,0 | E |
| Li | 8,630 | 5,640 | A | 1,380 | 0,900 | A |
| Mg | 231,6 | 193,4 | ABC | 118,4 | 223,4 | ABC |
| Mn | 151,4 | 144,1 | A | 67,73 | 89,40 | ABC |
| Mo | 143,4 | 131,4 | A | 283,8 | 252,2 | CD |
| Ni | 159,0 | 126,3 | A | 22,53 | 21,69 | A |
| Pb | 57,89 | 62,51 | A | 8,790 | 9,360 | A |
| Sb | 482,6 | 290,0 | CD | 1506 | 904,6 | E |
| Tl | 28,91 | 51,60 | A | 31,05 | 59,11 | AB |
| V | 5,270 | 6,690 | A | 2,380 | 3,020 | A |
| Zn | 953,0 | 791,5 | E | 369,0 | 387,3 | D |
| Se | 5889 | 3385 | G | 55,93 | 39,28 | AB |

Table 8. Cluster identity and factor loadings of three factors identified in Factor analysis for the element on leaves during the whole sampling period. In Bold are the chosen loadings.

| | Cluster | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|---|
| Al | 1 | 0.44 | 0.38 | **0.54** |
| Mg | 1 | 0.15 | 0.47 | **0.67** |
| Ba | 1 | -0.07 | -0.09 | **0.80** |
| Ca | 1 | 0.10 | 0.44 | **0.75** |
| Cd | 1 | 0.55 | -0.43 | **0.66** |
| Ni | 1 | 0.21 | 0.13 | **0.69** |
| Cr | 1 | **0.95** | 0.21 | 0.03 |
| Cu | 1 | **0.84** | 0.35 | 0.07 |
| Li | 1 | **0.92** | 0.21 | 0.11 |
| Pb | 1 | **0.69** | 0.31 | 0.11 |
| Sb | 1 | **0.56** | 0.50 | 0.07 |
| Se | 1 | **0.78** | 0.33 | 0.32 |
| V | 1 | **0.37** | -0.06 | 0.03 |
| K | 1 | 0.09 | **0.59** | **0.51** |
| Co | 1 | -0.10 | **0.61** | 0.59 |
| Mn | 1 | 0.10 | **0.35** | 0.03 |
| Mo | 1 | 0.31 | **0.50** | 0.04 |
| Tl | 1 | 0.09 | **0.35** | 0.20 |
| Fe | 2 | 0.25 | **0.81** | 0.11 |
| As | 2 | 0.07 | **0.81** | 0.26 |
| Zn | 2 | 0.18 | **0.49** | -0.01 |

# Paper III

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## Particulate matter and element accumulation on coniferous trees at different distances from a highway

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**Abstract**

*Picea sitchensis* (Bong.) Carrière, (one and two year old needles) and *Pinus sylvestris* L., (one year old needles), were tested for their capacity to accumulate particulate matter on the leaf surface or in waxes on the leaf surface. Element accumulation on needle surfaces was also analysed. Sampling was carried out at four distances from a heavily trafficked road in South Western Norway in October 2012. *P. sitchensis* accumulated a higher quantity of coarse PM compared to *P. sylvestris. Deposition* of all fractions of PM increased with time, with largest amounts on two year old as compared to one year old needles of *P. sitchensis*. Surface content of 14 out of 25 analysed elements were highest in *P. sitchensis* compared to *P. sylvestris*. A higher accumulation of coarse PM and elements therein (in 14 of 25 elements), was observed closest to the road as compared to larger distances.

Key words: Air pollution, Deposition trend, Enrichment Factor, *Picea sitchensis*, *Pinus sylvestris*

**Introduction**

Air pollution is a serious problem in the urban environment, causing diseases and premature deaths (WHO, 2005; Sawidis et al., 2011). Particulate matter (PM) is the principal component of anthropogenic air pollutants that comprise a mixture of heavy metals, black carbon, polycyclic aromatic hydrocarbons and other substances (Bell et al., 2011). Traffic is the most important source of particulate matter in urban areas, both because of the combustion of fuels and the wear of roads and mechanical parts of cars (Oliva and Espinosa, 2007). PM is classified according to the particle diameters (Power et al., 2009), coarse PM10 (2.5 - 10 µM), fine PM2.5 (0.1 - 2.5 µM) and ultra-fine PM 0.1 (< 0.1 µM). Many studies address only elements (Rucandio et al., 2011; Simon et al., 2011) or only PM, without the analysis of the chemical composition of this (Dzierzanowski et al. 2011; Sæbø et al., 2012). Because of their capacity to accumulate contaminants on leaves and bark, plants have also been used to monitor environmental quality (Espinosa and Oliva, 2006; Kardel et al., 2010; Serbula et al., 2012). The large leaf surface area and the transpiration process of plants permit the adsorption and absorption of both particulate and gaseous contaminants (Nowak et al., 2000; Bealey et al., 2007). Hence, it has been suggested that vegetation may play a role in improving the local air quality (Nowak et al., 2006). The pollution mitigation capacity by vegetation has been estimated for whole cities or urban areas but often with considerable uncertainty in results (Tallis et al., 2011). In the aforementioned study, the urban canopy of London has been estimated to remove annually between 0.7% and 1.4% of PM10 product by the urban boundary layer (852-2121 tonnes). Considering an increase of tree cover up to 20- 30%, the deposition of PM10 increase until 1.1–2.6% (1109-2379 tonnes). Given the complex relationships between how vegetation structure and meteorological conditions affects dispersion and deposition of contaminants, the effects of vegetation on air quality may be less evident than anticipated (e.g. Buccolieri et al., 2009, Vos et al., 2013, Setälä et al., 2013). It remains to be documented under what circumstances and at what scales vegetation may capture enough particulate matter to improve air quality and under what circumstances vegetation has no or maybe even a negative effect on air quality (Buccolieri et al., 2009). Species specific characteristics like vegetation structure, plant height, leaf surface, leaf area index, leaf microstructure and the diameter and shape of particulates are important (Fowler et al., 2003, Räsänen et al. 2013). Also meteorological parameters, as precipitation, wind speed, turbulence and air humidity, are important factors (Litschke and Kuttler, 2008; Winkler, 1988) interacting with vegetation design and structure. To maximize the efficiency of plants in air pollution mitigation, plant choice, design and their interaction are probably very important. But we haven't found quantitative studies that document those aspects. Conifers like *Pinus* species are considered good PM accumulators (Beckett et al. 2000; Freer-Smith et al., 2005; Sæbø et al., 2012), but we lack knowledge about relative performance of different conifers, the effects of needle age and effect of distance from the source of pollution. Therefore we compared accumulation of elements and particulate matter on leaf surfaces of two conifers, *Picea sitchensis* and *Pinus sylvestris*, at increasing distances from a heavily trafficked road as a pollution source. We consider such knowledge to be important for the future planning of green infrastructure, aiming at capturing airborne pollution. We tested the following hypotheses: 1) The two species differ in accumulation of pollutants on needle surface, 2) Two year old needles accumulate more PM and metals than one year old needles (*Picea sitchensis*), 3) The amount of intercepted pollutants decrease with distance from the road, 4) The traffic emissions can be identified as source of pollutants in the study area.

**Methods**

*Study area and needle sampling*

Needles of *Picea sitchensis* ((Bong.) Carrière), and *Pinus sylvestris* L., were collected in October 2012 in a forest adjacent to a heavily trafficked motorway (E 39), close to Stavanger, Norway (N 58°55' E 005°42'). The road is characterized by an average daily number of 65 000 vehicles and traffic probably represents the major source of pollution (meteorological conditions of the area is given in Table 1). The area is close to the sea and is characterized by frequent winds from the North Sea. This situation causes most of the time a PM flux from the road to the forest of our study (east of the road). Needles of *Picea sitchensis* (first and second generation needles) and *Pinus sylvestris* (first generation needles only) were collected on the south-eastern side of the highway, at four distances from the road verge (distance 1: 1-10 m;  distance 2: 20-30 m; distance 3: 30-40 m; distance 4: 70-90 m). In *P. sylvestris,* the needles of second generation were missing and only the youngest needles were collected. Needles from 4 replicate trees per species were sampled per needle generation and per distance from the street. A total of 48 samples were collected. Leaves contaminated with pests or diseases were not used for analysis. The samples were collected at 1 to 2 meters above the ground. In the laboratory, branches were separated into one and two year old needles (in *P. sitchensis*). Samples were dried at 40 °C for 3 days. In order to avoid the interference between the handling of the samples and results, needles were carefully removed from the twigs, using a glass rod.

*Element composition of soil*

Ten sub-samples of top-soil were collected from 70 to 90 m from the road, in order to use as reference soil for the calculation of the enrichment factor (EF). Each sub-sample (200 g) was collected at a depth 0 to 10 cm. During sampling, surfaces in open areas, free from shrubs and tree vegetation were chosen in order to avoid direct influence of the leaf debris onto the element soil content (Skrbìc et al., 2012). Soil sub-samples were dried at room temperature until a constant weight. Aggregates of the soil were ground using a ceramic mortar and pestle and then sieved using an element sieve in order to eliminate particles larger than 2 mm. Fifty grams of each sub-sample of soil were combined in order to represent the soil furthest from the source of pollution (control soil).

*Accumulation of PM and wax quantity on needles*

PM on the leaf surfaces (water soluble) and in the waxes (soluble in chloroform) and the wax quantity (washed off by chloroform), was analysed as reported in the literature (Dzierżanowski et al., 2011). The only change to the protocol was that the drying time of filters was increased from 30 to 60 seconds. The leaf area of every washed sample was then measured using Epson Perfection

V7000 scanner (Epson, USA Inc.), and calculated by the WinRhizo software (Regents Instruments Inc., Quebec, Canada). The amount of PM was expressed per unit area ($cm^2$) of one side needle surface. This allowed us to distinguish between PM on the surface (SPM) and in the waxes (WPM) and to calculate the total PM of the different size fractions, summarized for surfaces and waxes (SWPM). Observations of the leaf surface presence of PM, on the abaxial or adaxial side were carried out using a Quanta 200, Environmental Scan Electronic Microscope (ESEM), FEI, with 70–300 times enlargement.

*Accumulation of elements on needles*

Needle samples of 1 g were washed as described in a previous work (Dzierżanowski et al., 2011). Fifty ml of distilled water and 30 ml of chloroform were used for washing, in order to maintain a similar ratio between needles and washing solutions. Particles larger than 100 µm were eliminated by sieving. Water and chloroform solutions, of each sample, were mixed and reduced at 70°C to 10 ml to obtain one solution phase. The solutions were digested using a Heating digester (DK 6, Velp® Scientifica, Italy), at 110°C per 60 minutes adding 12 ml of a mixture of $HNO_3$ (65%) and $H_2O_2$ (30%) (10:2) v/v. A water cooling system was mounted to reduce the loss of elements by evaporation. Finally, the volume was adjusted to 25 ml with distilled water. Content of 25 elements (Li, Be, B, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Ga, Ag, Cd, Cs, Ba, Pb, V, Zn, Rb, Sr, Sb), was analysed at Buzzi Laboratories, Prato (Italy, ISO 17025 certified), using a 7500 Series, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Agilent (USA). Digestion and analyses of blanks was performed using the same protocol. The results of element contents were expressed per unit area of needle surface.

*Element analysis of soil*

Two parallels of 0.5 g were separated from each of the two composite samples. Digestion was performed applying 24 ml of the acid mixture aforementioned at 110°C for 60 minutes. After that, another 24 ml of the same acid mixture were added and a second cycle of digestion was initiated.

Solutions were filtered through ashless filter papers, pore size 8 µm, (Whatman™, US), and then the volume was adjusted to 100 ml using distilled water. Analysis of elements was accomplished following the same protocol used for the SWPM element content. Digestion of blanks was also performed.

*Enrichment factors of elements on needles*

The enrichment factor (EF) of elements in leaf samples relative to the abundance of Al was estimated (Lorenzini et al., 2006). We compared EF estimates using both the element composition of control soil (Skrbìc et al., 2012) and the average crustal element composition reported by Taylor and McLennan (1985) as references. Analysis of variance (One-way Anova) was carried out on the two datasets of EF separately. More than one criteria was used to interpret the results of EF analysis (Aničić et al., 2001; Serbula et al., 2012). In the present study, all elements with EF statistically different from the first Homogeneous group (LSD test) were considered indicators of enrichment. In addition, to achieve an unequivocal result, only the elements enriched using both control soil and soil crust references were considered as “significantly enriched”.

*Statistical analyses*

Samples of needles were collected from four individual trees for each species and at each distance range from the road. Differences in PM accumulation between species, needle ages and distances from the road were tested with analysis of variance (ANOVA) (STATGRAPHICS Centurion XV.II, StatPoint Inc., Warrenton, Virginia, USA). Fisher's least significant difference (LSD) procedure was used to discriminate among the means. The outliers were identified using scatter plots and residuals plot and removed from the dataset. Thus, four outliers of 288 values were removed from the dataset of PM and twenty-four of 1175 values from the dataset of elements. The relationships between accumulation of PM10 and elements and distance from road were tested in multiple regression analysis separately for each element. The relationships between the different elements were tested with correlation analyses. Cluster Analysis (CA), was performed using the Ward method and Euclidean distance as metric (Oliva and Espinosa, 2007). Factor Analysis (FA) with varimax rotation was applied to the whole dataset elements on leaves. Results of correlations, CA and FA were compared in order to find the probable sources responsible for the observed elemental accumulation on leaves.

**Results**

*Accumulation of PM and wax quantity on needles*

Deposition of air pollution on the leaves of conifers was affected by species, needle age and distances from the road, but the different size fractions showed contrasting patterns (Table 2., Fig. 1). Accumulation of PM10 decreased with distance from the road in both *Pinus sylvestris* and *Picea sitchenisis*, while the smaller fractions did not show any clear trends with respect to the distance from the road (Fig. 1). Similar results were obtained in *Picea* (both year age) and *Pinus*. *Picea* had 26 % higher accumulation of total PM10 on the youngest needles as compared to *Pinus*. No differences were found between the species for the smaller PM fractions (Table 2). *Picea* had 34 % lower PM deposited on the youngest needles as compared to the older leaves (Table 2.). The quantity of waxes on leaves didn't differ between species, needle generations or the different distances from the road (data not shown). Correlation analysis between wax content and the PM in the wax layer did not shown significant relationship. Anyway a positive correlation (r=0.61), was found between the total accumulation of PM in the wax layer (Tot WPM) and the total accumulation of particulate matter on the leaf surface (Tot SPM). A positive correlation was also found between total PM10 and total PM2.5 (r=0.54).

*Accumulation of elements on needles*

Elements were present in different quantities. The order of deposition of elements was K > Ca > Fe > Na > Al, Mg, Pb > Mn, Cu, B, Cr > all the others. Differences in element accumulation between species were found in 14 of 25 elements. In all these cases the element content was higher in *P. sitchensis* first year old needles compared to *P. sylvestris* with the exception of Mg. Differences in element accumulation between 1 and 2 year old needles of *P. sitchensis* were observed only in Co, Mn, and K with respectively 36 %, 62 %, and 27 % higher quantities in the older needles. Since the two generations of needles of *P. sitchensis* had very similar element deposition, the data were pooled and analysed statistically to investigate the differences in elements accumulation by distance from the road. Higher concentrations of 14 of the 25 elements were found in *P. sitchensis* close to the road compared to the other distances (Table 3), while no significant differences or trends were discovered in *P. sylvestris* for single elements (Table 4). Multiple regression analysis showed that accumulated particulate matter and distance from the road explained a large part of the variation in concentration of several of the elements (Table 5). The highest $r^2$ values were found in Ba (54), Ga (52) and Be (55). Element accumulation increased with accumulation of particulate matter and decreased with distance from the road (Table 5).

*Enrichment factors of elements on needles.*

EFs estimated using the element composition of control soil gave a higher number of enriched elements compared to those calculated using the element composition of the upper crust (Table 6). Ag, Cd, Pb and Zn, were enriched in both datasets.

*Element source identification using multivariate methods.*

Cluster analysis grouped the elements in three principal clusters whilst, factor analysis, indicated that approximately 65% of the variance may be explained by the first three factors (Table 7). Factor 1, 2 and 3 accounted for 42%, 12% and 10% of the total variance, respectively. Only positive correlations were found between the different elements on needles (Table 8), especially between Ga and Ba (r=0.99) and V and Cr (r=0.93). The number of factors and of clusters may indicated the presence of three different sources for the studied elements. The high number of positive correlations indicated that the elements have the same source/s (Monaci et al., 2000).

## Discussion

*Accumulation of PM on needles*

*P. sitchensis* and *P. sylvestris* showed different capacity in PM accumulation, partially supporting our first hypothesis. Conifers with their smaller leaves and more complex shoot structures, are considered more efficient than broad leaf trees in capturing PM (Freer-Smith et al., 2005). The higher quantity of total PM10 on *P. sitchensis* may partially be attributed to the smaller size of the trees' needles compare to *P. sylvestris.* In addition, *Picea* species have a higher leaf area index (LAI) than *Pinus* species (Gower and Norman, 1991). These features and conditions causing high air turbulence inside the tree crowns, contribute to increase the interception capacity of contaminants by conifers plants (Bunzl et al., 1989). The amount of PM accumulated by *P. sylvestris* (32.99 µg $cm^{-2}$) is in line with results early reported (Sæbø et al., 2012), for the same species (~40 µg $cm^{-2}$), recorded in a plot only one km away from that of the present research. The highest content of PM fractions found in the two year old needles in *P. sitchenisis,* support our second hypothesis. This partially contrasts with what reported in a previous research (Nowak et al., 2006) where was supported that leaves are only a temporary retention site for particulate matter. The presence of algae or fungi on needles may increase the weight of the total PM, especially because the two year old needles are affected by more shade than the youngest needles. Observations at ESEM showed small amounts of an unidentified fungal mycelium on the needles surfaces of both species.  Also PM was observed (Fig. 2). This underlines the importance of analysis of other factors in addition to PM. The decrease in total PM10 in *P. sitchensis* and *P. sylvestris* at increasing distance from the road partially confirm our third and fourth hypothesis. The fact that only the total PM10 fraction showed a clear trend may be explained by differences in Deposition Velocities ($V_{ds}$). As early studied (Fowler et al., 2003), $V_{ds}$ (mm $s^{-1}$) indicates the efficiency in deposition of PM and with increasing size of PM above 0.1 µm, will correspond to an increase in $V_{ds}$. Increasing values of $V_{ds}$ will lead to  a higher capacity of particle interception by plants. We have shown that total PM10 is mainly deposited close to the road, maybe because of its higher $V_{ds}$ compared to the smaller fractions. Thus, the smallest fractions of PM may be dispersed over larger areas, which caused the lack of differences among distances in our study.

*Accumulation of elements on needles*

Elements analysis was performed with the aim of studying the behavior of another kind of air pollutants in addition to PM. A similar sequence of elements (K, Ca, Na, Mg and Fe), to that we found, was in needles of *Pinus halepensis* in the urban area of Gela, Italy (Bosco et al., 2005). A similar relationship between the quantities of elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) was also found also in Bosnia and Herzegovina at different distances from a heavily trafficked road (Skrbìc et al., 2012). These results also support our fifth hypothesis: the difference in quantities between elements we found, is probably typical of a traffic polluted area. This is also confirmed by the higher concentrations of elements observed close to the road. The higher presence of 14 out of 25 studied elements in *P.sitchensis*, partly support our first hypothesis for differences between species. The low differences in element accumulation (Co, Mn, K), between one and two year old needles of *P.sitchensis*, don't support our second hypothesis for the element deposition. In an earlier study (Suchara et al., 2011), a higher content of elements was found in two year old needles of *Picea Abies* compare to one year old needles. The fact that we didn't find difference in element accumulation between 1 and 2 year old needles of *P. sitchensis*, could be due to the difference in species and to the larger precipitation at the site of our research which cause a larger wash off effect. Another important factor could be that in our study only the elements deposited on the leaf surface were analysed whilst in the aforementioned work whole needles were analysed. Regarding the trend of deposition at the different distances, elements seem to follow the same trend as total PM10 accumulation, confirming also the third and fourth hypothesis. In *P. sitchensis*, 14 of 25 elements were found in higher concentrations near the road as compared to further away. Even if not confirmed by significant differences, similar trend was observed also in *P. sylvestris.* The relative content of elements increases with the increasing size of particles (Li et al., 2003 and

Araujo and Nel, 2009). This could explain why elements show a positive relation only with PM10. The Matrix of correlation between elements (Table 8) shows several positive correlations, for example between Ga and Ba (r=0.99) and V and Cr (r=0.93). The correlations between elements suggest that these elements originate from the same sources (Monaci et al., 2000). The results of multiple regression analysis, with the high number of significant results (17 of 25), suggest that presence of elements on leaves is negatively dependent on the distance from the road and positively dependent on total PM10, which probably is the main carrier of the elements. However, deposition of naturally occurring PM and the presence of fungi (Fig. 2), probably influence also the composition of elements at this site.

*Enrichment factor of elements on needles and element source identification using multivariate methods*

We found that dust on needles was enriched in Ag, Cd, Pb and Zn and thus may originate from a different source than soil. Cd, Pb and Zn are typically associated with traffic pollution (Peachey et al., 2009; Monaci, 2000), supporting our fourth hypothesis. The ocean is a possible source of Ag (Lanceleur et al., 2013). Al, which is considered to be a crustal element (Jancsek-Turóczi et al., 2013), was not enriched, confirming its role as indicator of soil content. The relationship of Ca, Cr, Mg, Na, Sr and V are confirmed in the different multivariate methods. These elements are grouped in the same cluster and presented high loadings in factor 3 (Table 7.), and are also highly correlated with each other. Al, Be, Co, Cu and Li are in the second cluster and in factor 1. Also in this case, a high number of correlations were found between the elements. Finally, Ba, Cs, Ga, K and Rb were in the third cluster, with high loadings in factor 2 and also with a large number of significant correlations. Three groups were created based on these results: group 1 (Ca, Cr, Mg, Na, Sr, V), group 2 (Al, Be, Co, Cu, Li) and group 3 (Ba, Cs, Ga, K, Rb). Group 1, which is characterized by elements found in sea water (Na, Mg, Ca and Sr), (Turekian, 1968), was interpreted as "Marine group". Group 2 was identified as "Soil group" because of the presence of Al which typically indicate the soil contribution (Lorenzini et al., 2006; Zhao et al., 2006). Finally group 3 may be related to the traffic emissions, as indicated by the presence of Ba, Ga, K and Rb (Grieshop et al., 2006; Fabretti et al., 2009; Apeagyei et al., 2011). Many of the elements can be attributed directly or indirectly to the traffic emissions (Pant and Harrison, 2013). However, some of the elements may originate from soils (Monaci et al., 2000). This demonstrates the importance of evaluating and discussing possible sources of contaminants. EF results didn't coincide whit results of multivariate analysis. Neither one of the enriched elements (EF analysis) is among the elements for which the source was identified (multivariate analysis). This can be explained considering the different nature of the performed analysis and the high level of restrictiveness applied in both the cases. The fact that two methods of EF calculation and three multivariate methods have been compared, made the results more reliable but brought to exclude a high number of elements, especially in EF analysis. The high level of restrictiveness adopted, made more difficult the coincidence of results between EF analysis and multivariate methiods.

We have demonstrated that *P. sitchensis* and *P. sylvestris,* with different efficiencies, are able to intercept PM10 and elements from highway related pollution, and that both particulate matter and element accumulation on needles decrease with distance from the road. This study shows the potential benefits of conifers in urban infrastructure, aiming at the increase in pollution deposition in vegetation along roads. Vegetation in urban areas should be designed so that the positive effects on air quality can be optimized. The highest deposition of air pollutants can be expected where the concentrations are highest. Our results suggest that green infrastructure may give best effect on pollution deposition when placed close the sources of pollution. However, the design and placement of vegetation should be made with care, so that decrease in local air flow doesn't increase pollution concentrations (Buccolieri et al., 2009). There is a need for research on how vegetation should be placed and designed in the urban landscape, in order to obtain efficient mitigation of air pollution.

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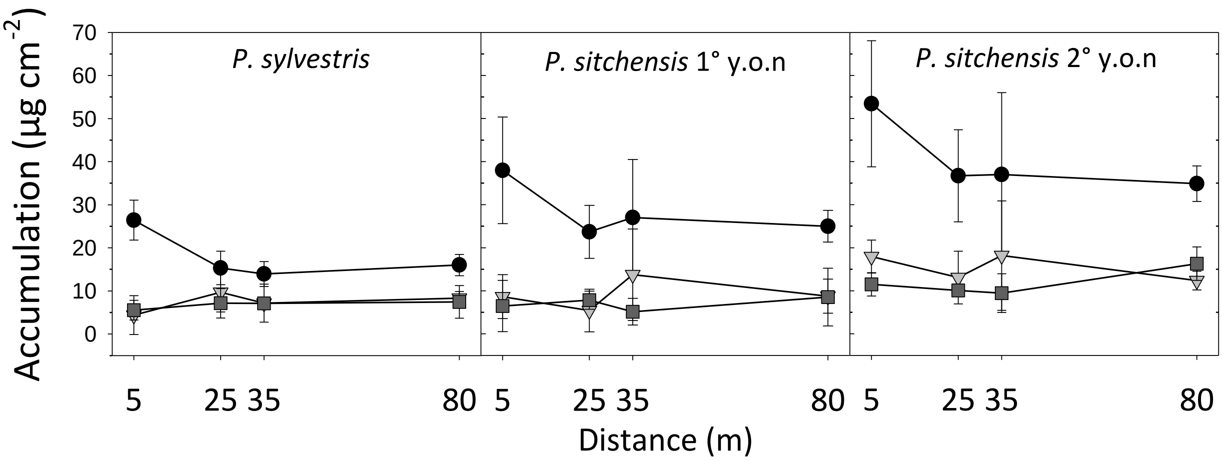
Table 1. Meteorological data for Stavanger (Våland: 1961 – 1990)

| Month: | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | Year |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pecipitation, mm | 99 | 75 | 80 | 51 | 68 | 79 | 96 | 113 | 161 | 154 | 151 | 123 | 1250 |
| Temperature °C | 1.2 | 1.1 | 2.8 | 5.5 | 9.9 | 12.8 | 14.1 | 14.4 | 11.7 | 8.8 | 4.8 | 2.5 | 7.5 |
| No days > 1 mm | 14.4 | 9.9 | 12.5 | 10.4 | 11.4 | 11.3 | 11.2 | 14.2 | 16.8 | 17.5 | 19 | 16 | 164.6 |

Table 2. Anova results of the accumulation of the different fractions of PM between *Picea sitchensis* I and II year old needles (above) and between *Picea sitchensis* and *Pinus sylvestris* I year old needles (below).

| *Picea sitchensis* one and two year old needles | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Year | | Distance | | Year x Distance | |
| | $r^2$ | *F* | *P* | *F* | *P* | *F* | *P* |
| Tot PM10 | 58 | 9.91 | 0.005 | 3.87 | 0.024 | 0.12 | 0.946 |
| Tot PM2.5 | 36 | 5.85 | 0.025 | 1.33 | 0.293 | 0.27 | 0.848 |
| Tot PM0.2 | 49 | 10.40 | 0.004 | 2.07 | 0.136 | 0.58 | 0.638 |
| *Picea sitchensis* and *Pinus sylvestris* one year old needles | | | | | | | |
| | | Species | | Distance | | Species x Distance | |
| | $r^2$ | *F* | *P* | *F* | *P* | *F* | *P* |
| Tot PM10 | 66 | 12.44 | 0.002 | 5.26 | 0.008 | 0.06 | 0.982 |
| Tot PM2.5 | 37 | 0.84 | 0.370 | 0.78 | 0.521 | 1.56 | 0.229 |
| Tot PM0.2 | 12 | 0.01 | 0.905 | 0.44 | 0.724 | 0.24 | 0.867 |




430 Fig. 1. Accumulation of different fractions of surface particulate matter (PM) on one year old needles of *P.sylvestris*, and of *P.sitchensis* (1°y.o.n) and two year old needles of *P. sitchensis* (2°y.o.n.), at different distances from the road (meters). PM is presented in total PM10 (dark circle), total PM2.5 (white triangle down) and total PM0.2 (black square). Values are means (µg $cm^{-2}$) ± SD.

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Table 3. Accumulation of elements on needles of *P.sitchensis* one and two year old needles at different distances from the road, expressed in meters. Data of elements are reported in µg $cm^{-2}$. Also shown are the results of one-way ANOVAs testing the effect of distance from the road on accumulation of each element.

| | Distance (m) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5 | | 25 | | 35 | | 80 | | ANOVA | |
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | *F* | *P* |
| Li | 0.876 | 0.428 | 0.334 | 0.415 | 0.145 | 0.042 | 0.274 | 0.179 | 8.98 | 0.001 |
| Be | 0.010 | 0.005 | 0.002 | 0.003 | 0.001 | 0.004 | 0.000 | 0.001 | 4.37 | 0.017 |
| B | 123.7 | 222.1 | 3.951 | 7.504 | 31.04 | 82.14 | 0.000 | 0.000 | 1.80 | 0.181 |
| Na | 1868 | 902.5 | 626.4 | 430.8 | 675.2 | 562.6 | 1042 | 536.7 | 5.53 | 0.006 |
| Mg | 674.5 | 212.8 | 240.1 | 142.7 | 187.0 | 64.76 | 397.8 | 262.0 | 6.76 | 0.003 |
| Al | 1224 | 584.7 | 516.7 | 344.7 | 233.5 | 116.6 | 339.5 | 160.7 | 13.98 | 0.000 |
| K | 4782 | 2013 | 4233 | 1369 | 2371 | 1072 | 3490 | 1630 | 2.89 | 0.061 |
| Ca | 2652 | 1700 | 1110 | 1314 | 1374 | 1507 | 1863 | 1449 | 1.64 | 0.216 |
| Cr | 30.29 | 21.80 | 48.49 | 46.10 | 27.16 | 21.17 | 14.50 | 8.757 | 1.51 | 0.245 |
| Mn | 352.4 | 240.2 | 332.6 | 311.3 | 236.7 | 167.9 | 291.1 | 227.9 | 0.23 | 0.872 |
| Fe | 1945 | 1220 | 1650 | 1593 | 455.8 | 467.8 | 967.7 | 525.1 | 2.49 | 0.090 |
| Co | 0.593 | 0.143 | 0.296 | 0.182 | 0.133 | 0.092 | 0.282 | 0.187 | 12.53 | 0.000 |
| Ni | 4.764 | 1.805 | 3.741 | 1.587 | 2.281 | 1.215 | 3.424 | 2.004 | 2.19 | 0.125 |
| Cu | 116.5 | 42.47 | 86.01 | 37.47 | 83.94 | 40.66 | 67.36 | 30.95 | 3.58 | 0.033 |
| Ga | 3.919 | 0.862 | 2.190 | 0.602 | 1.974 | 0.404 | 2.013 | 0.439 | 18.49 | 0.000 |
| Ag | 8.548 | 6.406 | 4.833 | 4.834 | 4.507 | 4.120 | 1.452 | 1.547 | 3.89 | 0.025 |
| Cd | 1.243 | 1.566 | 1.754 | 1.463 | 1.039 | 1.274 | 2.649 | 0.870 | 2.41 | 0.097 |
| Cs | 0.251 | 0.088 | 0.259 | 0.054 | 0.083 | 0.049 | 0.111 | 0.084 | 10.78 | 0.000 |
| Ba | 57.04 | 10.06 | 36.40 | 4.705 | 30.98 | 6.081 | 31.44 | 6.656 | 27.47 | 0.000 |
| Pb | 452.2 | 349.9 | 241.3 | 299.8 | 268.1 | 197.1 | 493.5 | 387.2 | 1.00 | 0.414 |
| V | 6.249 | 3.185 | 15.63 | 16.27 | 7.768 | 6.932 | 2.521 | 1.027 | 2.41 | 0.099 |
| Zn | 1347 | 2637 | 1766 | 2356 | 958.3 | 1075 | 522.2 | 438.0 | 0.64 | 0.598 |
| Rb | 8.295 | 3.388 | 8.030 | 2.845 | 3.300 | 1.055 | 4.764 | 3.061 | 4.50 | 0.014 |
| Sr | 15.37 | 5.787 | 5.850 | 3.723 | 5.944 | 1.916 | 8.490 | 4.898 | 6.71 | 0.003 |
| Sb | 1.206 | 0.941 | 0.341 | 0.659 | 0.041 | 0.056 | 0.080 | 0.061 | 6.10 | 0.004 |

Table 4. Accumulation of elements on one year old needles of *P. sylvestris*, at different distances from the road expressed in meters. Data of elements are reported in µg $cm^{-2}$. Also shown are the results of one-way ANOVAs testing the effect of distance from the road on accumulation of each element.

| | Distance (m) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5 | | 25 | | 35 | | 80 | | ANOVA | |
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | *F* | *P* |
| Li | 0.281 | 0.062 | 0.153 | 0.052 | 0.145 | 0.036 | 0.180 | 0.046 | 1.43 | 0.285 |
| Be | 0.004 | 0.002 | 0.001 | 0.001 | 0.001 | 0.001 | 0.000 | 0.000 | 1.47 | 0.276 |
| B | 33.38 | 22.76 | 69.55 | 69.55 | 11.02 | 11.02 | 83.32 | 83.32 | 0.35 | 0.788 |
| Na | 520.0 | 116.8 | 685.9 | 110.0 | 548.7 | 214.9 | 631.8 | 258.6 | 0.18 | 0.910 |
| Mg | 219.7 | 89.0 | 147.8 | 31.58 | 251.9 | 75.25 | 226.8 | 69.28 | 0.41 | 0.748 |
| Al | 807.5 | 382.1 | 369.5 | 134.38 | 345.7 | 75.12 | 301.6 | 82.28 | 1.26 | 0.331 |
| K | 1247 | 162.9 | 1420 | 86.19 | 1890 | 272.9 | 1855 | 449.6 | 1.32 | 0.315 |
| Ca | 925.9 | 436.3 | 627.3 | 232.7 | 2120 | 825.8 | 1541 | 424.7 | 1.59 | 0.242 |
| Cr | 25.00 | 10.80 | 18.28 | 4.910 | 12.01 | 2.076 | 31.73 | 20.61 | 0.65 | 0.599 |
| Mn | 63.44 | 8.460 | 69.00 | 20.62 | 72.29 | 9.706 | 67.59 | 33.06 | 0.03 | 0.992 |
| Fe | 1464 | 549.4 | 126.6 | 51.06 | 1181 | 494.1 | 410.4 | 215.4 | 2.67 | 0.095 |
| Co | 0.177 | 0.036 | 0.088 | 0.026 | 0.200 | 0.059 | 0.094 | 0.032 | 2.04 | 0.162 |
| Ni | 3.214 | 0.742 | 1.974 | 0.715 | 2.983 | 1.096 | 3.485 | 1.269 | 0.45 | 0.723 |
| Cu | 44.60 | 10.98 | 35.65 | 8.168 | 33.14 | 3.811 | 52.27 | 6.150 | 1.31 | 0.321 |
| Ga | 1.846 | 0.076 | 1.696 | 0.048 | 1.829 | 0.059 | 1.444 | 0.362 | 0.85 | 0.493 |
| Ag | 4.749 | 2.425 | 2.970 | 1.834 | 3.065 | 0.750 | 3.846 | 1.698 | 0.22 | 0.884 |
| Cd | 0.052 | 0.052 | 0.636 | 0.636 | 0.708 | 0.425 | 0.286 | 0.191 | 0.61 | 0.624 |
| Cs | 0.078 | 0.013 | 0.068 | 0.018 | 0.055 | 0.009 | 0.084 | 0.033 | 0.35 | 0.788 |
| Ba | 35.01 | 7.538 | 25.96 | 0.913 | 28.12 | 1.315 | 22.87 | 5.293 | 1.22 | 0.346 |
| Pb | 62.42 | 8.071 | 123.6 | 32.75 | 66.64 | 25.54 | 157.8 | 46.70 | 2.15 | 0.148 |
| V | 8.082 | 3.038 | 4.915 | 1.425 | 2.648 | 0.245 | 8.116 | 6.484 | 0.75 | 0.543 |
| Zn | 663.7 | 445.3 | 172.8 | 90.34 | 1159 | 762.7 | 682.0 | 410.9 | 0.68 | 0.582 |
| Rb | 2.495 | 0.515 | 3.650 | 0.338 | 2.753 | 0.282 | 3.931 | 1.299 | 0.89 | 0.473 |
| Sr | 5.193 | 2.710 | 2.520 | 0.678 | 6.223 | 2.049 | 5.495 | 2.454 | 0.58 | 0.639 |
| Sb | 0.570 | 0.058 | 0.034 | 0.023 | 0.173 | 0.105 | 0.028 | 0.028 | 0.68 | 0.582 |

Table 5. Multiple regression analysis showing how accumulation of the different elements depends on total accumulated particulate matter (PM10) and distance from road.

| | Model | | | Constant | | Tot PM10 | | Distance | |
|---|---|---|---|---|---|---|---|---|---|
| | *F* | *P* | r² | Coeff. | *P* | Coeff. | *P* | Coeff. | *P* |
| Ag | 5.98 | 0.005 | 22 | 5.34 | 0.032 | 0.081 | 0.088 | -1.284 | 0.033 |
| Al | 12.90 | 0.000 | 38 | 846.6 | 0.001 | 8.232 | 0.070 | -216.7 | 0.000 |
| B | 1.21 | 0.309 | 5 | 55.45 | 0.403 | 1.001 | 0.437 | -16.48 | 0.313 |
| Ba | 25.52 | 0.000 | 54 | 37.87 | 0.000 | 0.390 | 0.000 | -5.439 | 0.000 |
| Be | 24.99 | 0.000 | 55 | 0.002 | 0.305 | 0.000 | 0.000 | -0.002 | 0.001 |
| Ca | 3.14 | 0.054 | 13 | 101.0 | 0.899 | 37.24 | 0.016 | 156.0 | 0.425 |
| Cd | 1.03 | 0.365 | 5 | 0.942 | 0.238 | -0.007 | 0.651 | 0.215 | 0.266 |
| Co | 16.10 | 0.000 | 43 | 0.132 | 0.161 | 0.008 | 0.000 | -0.043 | 0.067 |
| Cr | 1.39 | 0.261 | 7 | 50.54 | 0.002 | -0.392 | 0.182 | -5.089 | 0.182 |
| Cs | 9.40 | 0.000 | 31 | 0.178 | 0.002 | 0.002 | 0.048 | -0.036 | 0.007 |
| Cu | 19.38 | 0.000 | 49 | 21.99 | 0.221 | 1.939 | 0.000 | -2.252 | 0.603 |
| Fe | 7.55 | 0.002 | 26 | 809.9 | 0.160 | 30.11 | 0.009 | -228.0 | 0.105 |
| Ga | 22.98 | 0.000 | 52 | 2.272 | 0.000 | 0.031 | 0.000 | -0.352 | 0.001 |
| K | 5.75 | 0.006 | 21 | 1849 | 0.054 | 53.12 | 0.005 | -134.3 | 0.556 |
| Li | 9.94 | 0.000 | 32 | 0.391 | 0.038 | 0.008 | 0.020 | -0.117 | 0.012 |
| Mg | 4.22 | 0.022 | 17 | 199.1 | 0.119 | 5.927 | 0.018 | -22.33 | 0.474 |
| Mn | 3.99 | 0.026 | 16 | 30.77 | 0.802 | 6.369 | 0.010 | 4.172 | 0.888 |
| Na | 6.30 | 0.004 | 23 | 519.5 | 0.165 | 20.82 | 0.006 | -80.39 | 0.375 |
| Ni | 2.12 | 0.133 | 9 | 2.709 | 0.016 | 0.035 | 0.103 | -0.141 | 0.596 |
| Pb | 2.19 | 0.124 | 10 | -24.09 | 0.885 | 6.533 | 0.048 | 44.20 | 0.281 |
| Rb | 4.06 | 0.024 | 16 | 5.962 | 0.001 | 0.045 | 0.191 | -0.811 | 0.062 |
| Sb | 12.38 | 0.000 | 37 | 0.587 | 0.061 | 0.013 | 0.028 | -0.247 | 0.002 |
| Sr | 4.76 | 0.014 | 19 | 4.940 | 0.100 | 0.143 | 0.016 | -0.613 | 0.399 |
| V | 1.26 | 0.293 | 6 | 14.38 | 0.005 | -0.113 | 0.234 | -1.639 | 0.177 |
| Zn | 1.80 | 0.178 | 8 | 390.1 | 0.673 | 28.64 | 0.115 | -88.85 | 0.693 |

Table 6. Comparison of the leaf enrichment factors (EF) calculated with the elements composition of control soil, and the average of the element composition of the upper crust as reference materials. Homogeneous groups (HG), derived by the multicomparison test of means tested by Least Square Difference test. Elements marked with shaded color are considered to be enriched by use of both enrichment methods.

| EF | Control soil | | | Average upper crust | | |
|---|---|---|---|---|---|---|
| | Mean | SD | H.G | Mean | SD | H.G |
| Ag | 548.85 | 426.1 | H | 14153 | 10987 | D |
| Al | 1.000 | 0.000 | A | 1.00 | 0.000 | A |
| B | 109.3 | 112.9 | BCDEF | 1720 | 1777 | AB |
| Ba | 19.22 | 10.84 | AB | 13.71 | 7.730 | A |
| Be | 0.380 | 0.280 | AB | 0.230 | 0.210 | A |
| Ca | 39.08 | 33.82 | ABC | 10.24 | 8.860 | A |
| Cd | 124.3 | 101.8 | DEF | 5521 | 4523 | C |
| Co | 0.670 | 0.380 | A | 4.540 | 2.570 | A |
| Cr | 60.24 | 44.88 | ABCD | 130.8 | 100.8 | A |
| Cs | 1.050 | 0.750 | A | 6.990 | 5.010 | A |
| Cu | 178.1 | 113.6 | F | 607.6 | 387.6 | A |
| Fe | 1.200 | 0.970 | A | 4.580 | 3.700 | A |
| Ga | 7.550 | 4.140 | A | 28.78 | 15.77 | A |
| K | 89.82 | 61.29 | CDE | 22.97 | 15.68 | A |
| Li | 0.390 | 0.210 | A | 2.710 | 1.490 | A |
| Mg | 5.950 | 3.970 | A | 4.570 | 3.050 | A |
| Mn | 1.120 | 1.130 | A | 71.98 | 72.33 | A |
| Na | 87.22 | 66.58 | CDE | 6.000 | 4.440 | A |
| Ni | 12.50 | 8.050 | AB | 36.60 | 23.57 | A |
| Pb | 190.3 | 168.8 | F | 2460 | 2183 | B |
| Rb | 15.46 | 10.31 | AB | 8.490 | 5.660 | A |
| Sb | 134.3 | 129.7 | EF | 239.7 | 231.5 | A |
| Sr | 21.96 | 14.53 | AB | 3.950 | 2.620 | A |
| V | 7.300 | 6.220 | A | 19.090 | 16.26 | A |
| Zn | 371.6 | 456.0 | G | 2775 | 3404 | B |

Table 7. Cluster identity and factor loadings of the three factors identified in the factor analysis for the element on leaves during the whole sampling period.

| | Cluster | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|---|
| Ag | 1 | 0.78 | 0.02 | -0.22 |
| Al | 2 | 0.89 | 0.11 | -0.04 |
| B | 1 | 0.60 | -0.00 | 0.06 |
| Ba | 3 | 0.78 | 0.43 | 0.10 |
| Be | 2 | 0.87 | -0.08 | -0.07 |
| Ca | 1 | 0.32 | 0.40 | 0.57 |
| Cd | 2 | -0.18 | 0.47 | -0.25 |
| Co | 2 | 0.76 | 0.49 | 0.13 |
| Cr | 1 | 0.24 | 0.15 | -0.80 |
| Cs | 3 | 0.36 | 0.82 | -0.25 |
| Cu | 2 | 0.74 | 0.20 | -0.10 |
| Fe | 2 | 0.30 | 0.62 | 0.19 |
| Ga | 3 | 0.82 | 0.38 | 0.14 |
| K | 3 | 0.29 | 0.89 | 0.00 |
| Li | 2 | 0.90 | 0.15 | 0.11 |
| Mg | 1 | 0.49 | 0.51 | 0.51 |
| Mn | 2 | -0.03 | 0.72 | 0.02 |
| Na | 1 | 0.53 | 0.47 | 0.53 |
| Ni | 3 | 0.25 | 0.57 | 0.06 |
| Pb | 2 | 0.57 | 0.28 | -0.01 |
| Rb | 3 | 0.18 | 0.86 | -0.08 |
| Sb | 2 | 0.59 | 0.11 | 0.00 |
| Sr | 1 | 0.58 | 0.53 | 0.37 |
| V | 1 | 0.19 | 0.11 | -0.85 |
| Zn | 1 | 0.04 | 0.52 | 0.11 |

Table 8. Correlation matrix of accumulation of the different elements. Pearson coefficient (r) was estimated. Only the results with r coefficients above 0.7 are shown. All the data shown are significant with $p<0.001$.

| | Be | Co | Cu | Ga | K | Li | Mg | Na | Rb | Sr | V | Zn | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 0.78 | 0.77 | | 0.74 | | 0.83 | | | | | | | 0.70 |
| Ba | | 0.76 | | 0.99 | | 0.73 | | | | 0.70 | | | |
| Be | | | 0.74 | | | 0.80 | | | | | | | |
| Ca | | | | | | | 0.77 | 0.72 | | 0.76 | | | |
| Co | | | | 0.79 | | 0.85 | | | | 0.73 | | | |
| Cr | | | | | | | | | | | 0.93 | | |
| Cs | | | | | 0.85 | | | | 0.89 | | | | |
| Fe | | | | | | | | | | | | 0.80 | |
| Ga | | | | | | 0.77 | | | | | | | |
| K | | | | | | | | | 0.88 | | | | |
| Mg | | | | | | | | 0.79 | | 0.81 | | | |
| Na | | | | | | | | | | 0.82 | | | |

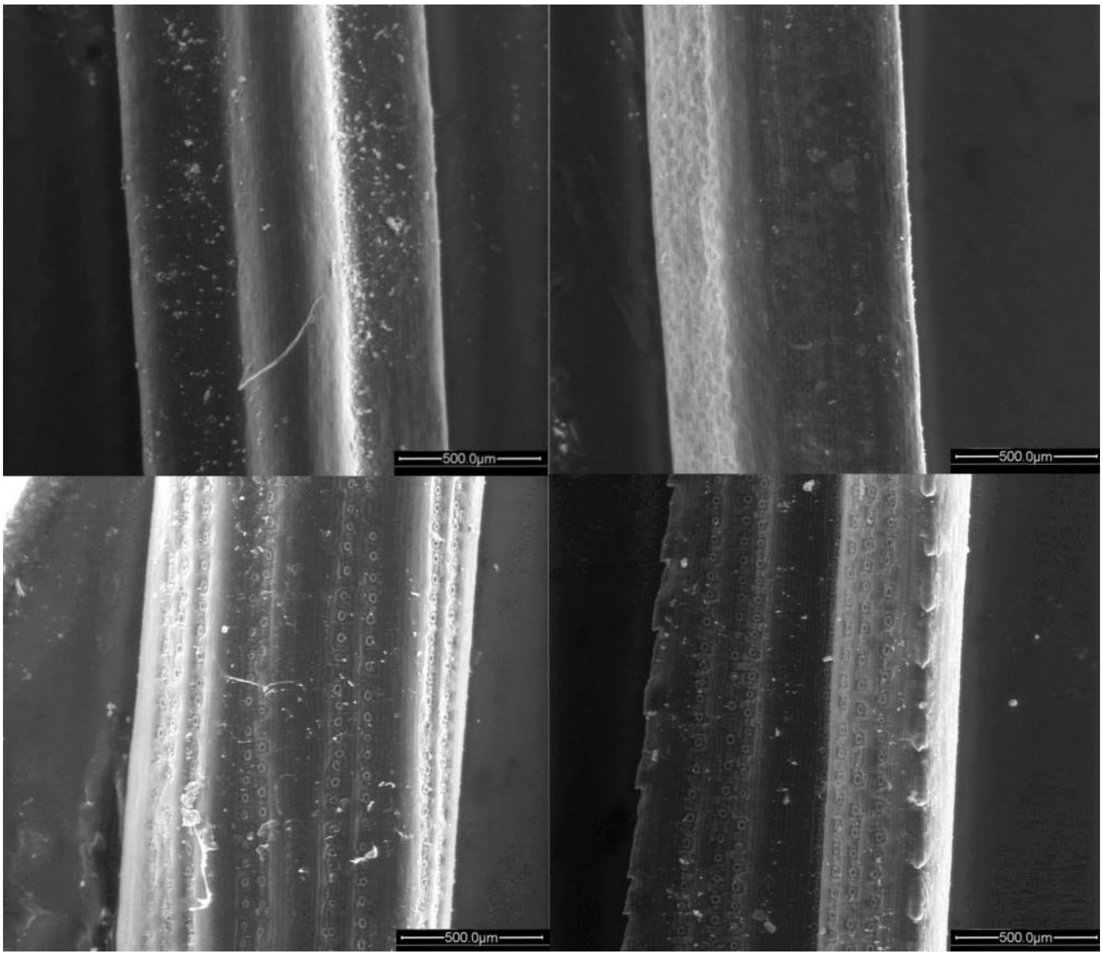


Fig 2. Adaxial and abaxial needle surface of *Picea sitchensis* (above) and *Pinus silvestris* (below).

## General discussion

The present work analyzed different aspects of the capacity of plants in mitigation of air pollution and $CO_2$ uptake. Nine evergreen woody plants species, two trees species and eight shrubs species, were tested. In paper 1, carbon uptake was investigated on the plants, grown in containers in order to better control the growth conditions, especially when drought stress was imposed. The aim of imposing drought stress was to simulate the urban environment of southern Europe during summer season, for which these species were studied. The results on carbon uptake of species differ depending on the availability of water. In fact, *E. x ebbingei* showed the higher $CO_2$ assimilation under optimal water availability, but its capacity decreased significantly under drought stress. *P. x fraseri* under drought stress showed the highest assimilation rate of $CO_2$. The use of containers probably led to different results than what would have been obtainable with adults plants grown in the ground, with a full expanded root system. However, the use of containers is necessary when simulating drought stress. In paper 1 is also reported a part relative to the capacity of the same shrub species (with the exception of *V. tinus*) in the accumulation on leaves surface of five heavy metals (Cd, Cu, Ni, Pb, Zn). This study was conducted on plants, grown in the ground close to a 4 lanes road. The aim of the aforementioned location of planting was to simulate the pollutant emissions of the urban areas. It was not possible to draw a clear conclusion on the accumulation of metals per unit leaf surface of different species. In fact only Pb, on five analyzed metals, was differently accumulated by species. *E. x ebbingei*, *L. japonicum* and *V. lucidum* showed the highest values. Considering what observed about the morphology of leaves surface and the growth parameters of plants, it was not possible to identify clear common characteristics of these species, which could explain these results. The observations of the leaves morphology at SEM did not include any kind of measure of specific characteristics (e.g. number of trichomes per unit surface, roughness of leaf surface), related to a better accumulation capacity of pollutants (Beckett et al. 2000). Then it was not possible to state for sure that there are not any characteristics which could explain the results. In order to distinguish among species for metal accumulation on leaves, a higher number of analyzed metals and replicates would have been necessary. Presence of elements was shown to change significantly in the three samplings carried out from late spring to early autumn. The influence of meteorological parameters on leaf deposition was confirmed by the PLSR analysis which shown how leaf depositions were negatively related with rain and RH% and positively related with wind speed and air temperature. To better study the trend of depositions during the season and the influence of meteorological parameters, a higher number of samplings and of measured elements would have been necessary. The metal content in the rain water collected under the plants, compared to that collected in a free area, confirmed the capacity of accumulation of plants and the capacity of rain in removing the leaf depositions, as was observed also by Nowak et al. (2006).

In Paper II, 13 elements out of 21 were differently accumulated by species on leaf surface. *E. x ebbingei*, *V. lucidum* and *P. x fraseri* showed the highest accumulations of elements per unit leaf area, and also the highest amounts of elements on the whole plant surface. As in the previous experiment, the depositions of elements per unit leaf surface were not explained by the observed morphological characteristics of leaves. On the other hand, these species had high values of Total leaf area, LAI, Height of plants and Crown diameter. It was then concluded that, in this study, the growth parameters, more than the morphological characteristics of the plants, influenced accumulation per unit leaf surface and per whole plant. Due to the higher number of samplings (6 instead of 3), and of elements (21 instead of 5), a more detailed information about the trend of elements on leaves were obtained. Also in this experiment the presence of elements increased from the start and then decreased until the end of the season (October). In addition, more solid results were obtained on the relations between pollutant depositions and meteorological parameters, partially confirming the results of the previous experiment. Rain was confirmed to cause a decrease of leaf deposition, as reported by Nowak et al. (2006), while wind speed was found to increase the presence of pollutants, as reported by Fowler et al. (2005). In contrast to the previous study, a clear influence of RH% and Air temperature on pollutants content on leaves was not found, even if these meteorological parameters were already observed to have an effect on leaf accumulation (Cavanagh et al., 2009; Fowler et al., 2003; Litschke and Kuttler, 2008) In addition, the concentration of an element in the air PM tends to increase the leaf depositions of the same element, confirming the close relation between PM and elements (Bell et al., 2011). These relations were also confirmed by the similar trend of PM on leaves as compare to that of elements. The trend of pollutants accumulations on leaves has been studied in several research projects. Anicic et al. (2011) found that a seasonal accumulation of pollutants on leaves (measured in May and September) can occur. We didn't find any studies reporting such details and such a high number of elements as we have on the leaf surface accumulations of shrubs in southern Europe. The study of the relations between this number of elements and meteorological parameters in an open field could represent another innovative characteristic of this work. In addition, as far as our knowledge, the use of Partial least square regression (PLSR) between element deposition on leaves and meteorological parameters was never used before. This kind of multiple regression, used both in paper 1 and 2, is recommended when a large number of related predictor variables is considered (Carrascal, L.M. et al., 2009). Also the Principal Component Regression (PCR) was tested with the same aim but, unlike the PLSR, the multi-co-linearity between the predictor variables posed difficulties in the analysis. Three different multivariate statistical methods permitted the identification of the possible sources of the pollutants. These methods have already been used (Bosco et al., 2005), but we didn't find any other research which compared this number of multivariate methods. The soil, in addition to the traffic emissions, was found to be responsible of the presence of some elements on the leaf surface. The high level of restrictiveness adopted in the interpretation of the results of multivariate statistical methods, and the high number of analyzed elements, improved the reliability of the results. The calculation of the Enrichment factor (EF) was made using two different reference materials (soil composition of the study site and the average composition of the global upper crust). The restrictive procedure used for the identification of the enriched elements led to a low number of considered elements and probably limited some critical point of this analysis (Reimann, C. and Caritat, P., 2000). Results of EF analysis are considered to be too dependent on the choice of reference material. In this work we used two different reference materials and the results of the different dataset were compared considering only the elements enriched in both methods. Consequently, the comparison of the results between EF analysis and multivariate methods was very strict. The use of three multivariate methods brought to more reliable and detailed results as compared to what found with EF analysis. Despite these facts, the use of different methods (multivariate methods and EF analysis) still appears to be a good approach to the critical interpretation of the results.

The results reported in Paper III indicated a higher capacity of *Picea sitchensis* compared to *Pinus sylvestris* in air pollutant accumulation on needles surface. These results derived by specific plants characteristics: *P. sitchensis* showed a smaller size, a higher number of needles and a higher LAI than *P. sylvestris.* These characteristics have been linked earlier to a better capacity in air pollution interception (Gower and Norman, 1991; Freer-Smith et al., 2005). *P. sitchensis* was able to accumulate a higher quantity of $PM_{10}$ and of several elements close to the road, and hedges of this plant may be able to limit the diffusion of pollutants from the source to the environment nearby. The fact that only $PM_{10}$ showed a significant decrease may have been caused by the lower deposition velocity which characterized the smaller fractions of PM compared to the larger one (Fowler et al., 2003). Cavanagh et al. (2009) studied the distribution of PM10 at different positions inside a green urban forest whilst Simon E. et al. (2011) studied the leaf concentration of some elements along an urban gradient in the city of Vienna. Both these studies found that pollution on plants tends to decrease with the increase in distance from the source. The measure of different kinds of pollutants on the leaf surface (different size of PM and several elements), at different distances from the hypothetical source of pollution, could represent something innovative in this field of research. By what found in the present work, the influence of the particle diameter in the distribution on leaves (Fowler et al., 2003) and the positive relation between particles size and their element content (Li et al., 2003; Araujo and Nel, 2009) were confirmed. $PM_{10}$ on the older needles increased during accumulation through the year. This partially contrasts with what reported on temporary presence of particulates on leaves (Nowak et al., 2006). The accumulation trend of $PM_{10}$ through the years was not confirmed in elements. This result demonstrates that considering more than one kind of pollutant can help to obtain more representative results. In this work, the same multivariate methods, already used in the paper 2, were used for the sources identification. The relationships among elements, which were showed by this analysis, were interpreted considering the possible sources in the neighboring area and the major wind direction. The assignment of every group of elements to a possible source was confirmed by literature data as in paper 2. The EF results were completely not comparable with the results of multivariate methods, because none of the enriched elements was present in the groups (multivariate methods).

## Conclusion

Earlier studies of the effect of plants on $CO_2$ sequestration and pollution mitigation were mainly conducted on trees (Sawidis et al., 2011; Nowak D.J. et al., 2013) while shrubby species have been often ignored. Trees represent a greater potential in terms of carbon storage and of pollution mitigation than shrubs. This is because of their higher woody biomass production ($CO_2$ storage) and their higher leaf surface (pollution mitigation). Despite this fact, the contribution of shrubs was found to be relevant (Jo and McPherson, 1995; Dzierzanowski et al., 2011; Sæbø et al., 2012). Recently a greater attention was paid on shrubs, especially regarding their capacity in intercepting air pollutants. Shrubs, due to the lower height of their crown, are more in contact with traffic emissions, filtering the near ground air. In addition, they require a minor space than trees having larger possibilities of collocation in urban areas. Aerodynamically, it was shown that the presence of trees in the street canyons can bring to a deterioration of the air quality by the reduction of the air exchange between polluting emissions and clean air (Buccolieri et al., 2009; Salmond et al., 2013). Shrubs can help to avoid this problem, representing an alternative to trees, even if trees can give benefits also to microclimate and energy consumption (Soares, A.L., et al., 2011). Most of the studies on pollution mitigation were conducted in north Europe whilst less shrub species were tested in Mediterranean areas. Lorenzini et al. (2006) and Espinosa and Oliva (2006) evaluated the capacity of bio-indicators of three shrub species in Italy and Spain, respectively. There is space for a broader screening of several species which characterizes the urban green areas of the city of Mediterranean basin. Paper I and II represent a contribution in this direction, providing information about the benefits in terms of $CO_2$ storage and pollution mitigation. Coniferous species are already known to be efficient accumulators of pollutants on their needles (Freer-Smith et al., 2005). Paper III represents a further contribution to the knowledge of coniferous species for their pollution mitigation capacity. In addition, the results on the distribution of the different pollutants from the road to the neighboring area can represent a contribution to the knowledge of the local pollution dynamics. Modelling studies quantified the beneficial effects of trees in pollution removal and in improvement of the air quality (Nowak et al., 2006; Bealey et al., 2007; McDonald et al., 2007). These studies provided important knowledge on the quantity and the economic value of the pollution removal by trees. On the other hand, the real local improvement of air quality has not been very well examined. Due to the nature of the modelling analysis, still quite large uncertainties remain on the real capacity of plants in significantly improving air quality. While confirming the fundamental role of modeling and hope for an increasing reliability of the results, future attention should be paid on the study of local improvement of the air quality. The deposition of pollutants increases when the concentration of pollutants is higher (Freer-Smith et al., 2005). The potential of pollution accumulation is probably better used when plants are closely placed to the local source of emissions. New design of plantation, conceived as a barrier against the local polluting sources, could be a new interesting step in this field. The results reported in this thesis may represent a contribution in this direction.

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