

Environmental Quality in Urban Allotment Gardens: Atmospheric Deposition, Soil, Water and Vegetable Assessment at LISBON City

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Received: 4 October 2017 / Accepted: 26 December 2017 / Published online: 16 January 2018
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Abstract The purpose of this study was to analyze the quality of atmospheric deposition, soil, vadose zone water, and plant species in several Urban Allotment Gardens (UAG) in the city of Lisbon, and to correlate its nature and characteristics with their location within the city pressures and with the farming practices, comparing results with similar studies elsewhere. Twenty one metals or metalloids (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Ta, V, Zn) and 16 PAHs (acenaphthene, acenaphthylene, anthracene, fluorene, phenanthrene, naphthalene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, indeno[1,2,3-c,d]pyrene), pyrene) were analyzed in the atmospheric deposition, and some of these elements/compounds were further analyzed in soils, water, and vegetables. Results show a wide range of concentrations in the city resulting from different soil types and contamination sources. Indexes based on ratios of selected PAHs suggest pyrogenic origins for the PAHs. Metals and metalloids have both anthropogenic and petrogenic origins, the latter mainly for soils with

vulcanic origin. Despite the fact that concentrations in soils and waters have exceeded the recommended values in some areas, the lettuce and cabbage rarely presented contamination, with the measured metal values generally under legislated limits, where this exist.

Keywords Urban allotment gardens · Heavy metals · PAH · Sources · Sinks

1 Introduction

Urban agriculture has received widespread attention in the last few years. Several European capitals have experienced a large increase in the number of land plots being used to grow vegetables either for own consumption or for selling in local markets (Bell et al. 2016). Although there has been a recent increase in the interest of local councils in regulating and encouraging urban agriculture, partly derived by the recent economic crisis, this type of agriculture has long been a part of the cities' history, like Lisbon (Henriques 2009). These allotments not only allow families to grow their own food products but also contribute to the general well-being of city inhabitants that have usually less contact with nature (Dunnett and Qasim 2000).

Besides proper and dedicated land areas allocated to urban farming by the municipalities, there is also an abundance of unregulated urban gardens that make use of any available and convenient patch of land, usually at the roadsides, even of major highroads like the example of CRIL, an inner ring road in Lisbon.

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The food safety of vegetables produced in an urban environment is often questioned due to its proximity to a range of city pressures including road traffic, aircraft corridors, fuel filling stations, heating systems, and industrial areas. Besides, past urban/industrial activities might have contaminated city soils, namely throughout air pollution deposition (Kabata-Pendias 2001; Morillo et al. 2007; Jean-Soro et al. 2015). In addition, the agricultural and in particular the horticultural land management practices themselves may lead to potential inputs from inadequate management of applied materials, such as fertilizers, composts and pesticides, as well as household items (e.g., fences, including materials such as paints or asbestos) (Hursthouse and Leitão 2016). These products can be an additional source of contamination for soil, water and edible vegetables, with harmful impacts on humans and other species. Moreover, the intrinsic soil concentration in certain elements can be high, depending on the chemical composition of the parent-rock (Kabata-Pendias 2001; Bechet et al. 2016).

Vegetables grown in urban areas can become contaminated either by absorption through the roots (when the soil or the water used in irrigation is contaminated) or by atmospheric deposition. Due to short lifecycle of most vegetables and the common habit of washing the vegetables before eating them, the latter factor is usually less important. Thus, of great concern in urban agriculture, is the transfer of substances like heavy metals, from the contaminated medium to the edible part of plants, contaminating the food chain and humans as end-users. Some metals, like Cd, Pb, and Cr are non-essential for plants but can be present in the environment due to anthropogenic activities. Others, like Cu and Zn, while essential for plants and animals can be toxic at high concentrations.

Several studies have been conducted regarding the risk of exposure to contamination from the consumption of vegetables grown in urban areas (Hough et al. 2004; McBride et al. 2014; Nabulo et al. 2012; Cruz et al. 2014). The results are highly site specific, due mainly to the incidence of local pollution, present and former presence of industry or other pollutant activities among other factors including soil and water contamination.

The objective of this study is to provide an assessment of urban allotment gardens (UAG) in Lisbon, through a comparative assessment of six case-studies. In particular, it was intended (i) to monitor the quality of dry and wet deposition, soil, vadose zone water, and

plant species and (ii) to correlate the city pressures, petrogenic origin and agriculture practices with the chemical status of atmospheric deposition, soils, water, and vegetables.

2 Materials and Methods

2.1 Global Characterization on the Urban Allotment Gardens

2.1.1 Location and Selection Criteria

This study was performed in the capital city of Portugal, Lisbon, having 547,700 inhabitants within its administrative limits, and around three million people in the metropolitan area (INE 2011). It has an area of 100 km² (5477 inhabitants per km²). The city of Lisbon has a typical Mediterranean climate with hot and dry summers being the precipitation concentrated between October and April. Long-term (1981–2010) mean annual rainfall is 572.8 mm and mean annual temperature is 16 °C (IPMA 2015).

In 2017, the total area of municipal urban agriculture including private and public areas is 31.8 ha, with 7.1 ha organized in 571 municipal parcels located on 14 Municipal Urban Allotments Parks (Mata 2014, 2017). The allotments present an average area ranging from 48 to 164 m² and a maximum annual cost of 1.5 € m⁻². Apart from these municipal urban farms, a multiplicity of unregulated allotments created by individuals or associations have been appearing occupying vacant lots, underutilized parks, and other open spaces. They are usually small sized (constrained by the available land) reflecting the use of existing land to enable self-sufficiency (Cameira et al. 2014).

The studied urban allotments were selected at six places within the city (Fig. 1) in consultation with the local municipality and according with the following criteria: (i) inclusion of soils with different geology in terms of permeability, geochemical background values, and capacity to reduce the concentrations of contaminants and (ii) inclusion of different urban pressures (roads, airport, etc.). From the six UAG, five are under the municipality control [PHVC (33,150 m², 38°44' 55.52"N, 9°7'30.51"W), LNEC (256 m², 38°45' 38.59"N, 9°8'39.99"W), CHPL (650 m², 38°45' 36.88"N, 9°8'43.49"W), QG (7000 m², 38°45' 6.29"N, 9°11'30.17"W), and PHG (5830 m², 38°45'

14.10°N, 9°11'29.76"W)), and one (CRIL, 4250 m²; 38°44'5.67"N, 9°12'24.85"W)] is unregulated.

2.1.2 Geology and Soil Type

Lisbon geological formations are described in the 1:10.000 geological map of Lisbon (Moitinho de Almeida 1986) (Fig. 1). In the UAG of PHVC, LNEC and CHPL, the geology includes Miocene formations (sand, clay and limestone) and the alluvial nature coverage of deposits associated with the valleys. The geological formations of QG and PHG are in a transition zone and include a mixture between volcanic nature rocks and sedimentary rocks from the Miocene. CRIL is located in the Volcanic Complex of Lisbon. A thin layer of soil, brought from an excavation site elsewhere, was added to PHG and PHVC.

2.1.3 Urban Pressures

A circular area with 1 km radius was defined around each AG and a detailed survey of the existing pressures

was performed. Data was input in a GIS to produce a map of soil occupation including road traffic, airports, cemeteries, etc. (Fig. 2). Road traffic deposition is the main common pressure, being the UAG from CRIL the most impacted and PHVC the least. Environmental impacts from Lisbon airport can also have an influence, especially in CHPL and LNEC. No previous industrial activity had occurred in the sites.

2.1.4 Agriculture Management Practices

The crops cultivated in the UAG are irrigated year-round especially in spring/summer due to the high temperature and evapotranspiration, and low precipitation. In autumn/winter, irrigation complements the precipitation inputs. Irrigation water comes from the public supply network in four of the studied allotments. In CRIL, it comes from precipitation and runoff water that is collected in reservoirs. In LNEC and QG irrigation, water is pumped from a well, although in QG water also comes from a spring. From in situ observation, it was clear that most farmers were over irrigating their crops. Apart

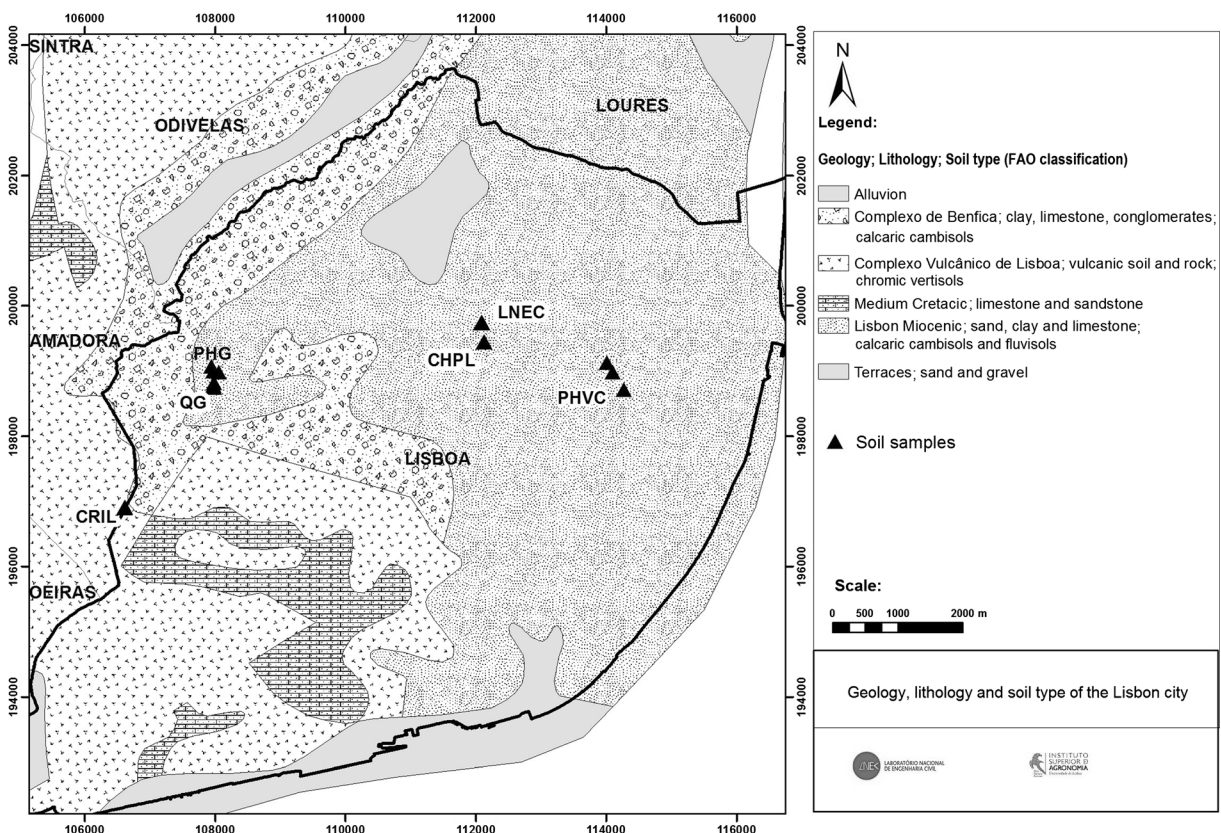


Fig. 1 Geological, lithological and soil type (IWG 2007) map of Lisbon city and location of the selected UAG

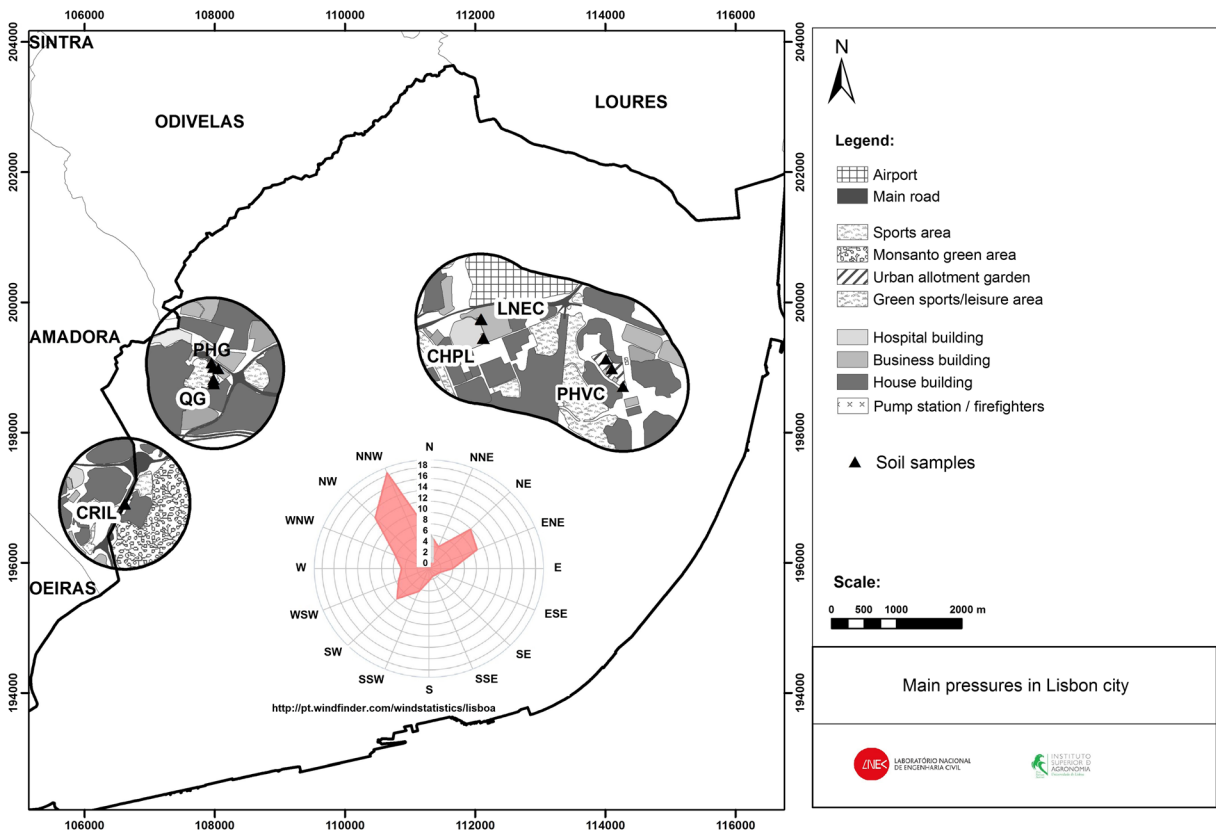


Fig. 2 Main pressures map of Lisbon city and wind direction distribution

from the chemical fertilizers, soil fertility is maintained by the application of different manures and bio composts.

2.2 Air, Soil, Water, and Vegetable Sampling Procedures

2.2.1 Dry and Wet Deposition

Dry and wet deposition was sampled in two distinct periods from 01/12/2015 to 6/17/2015 and 6/17/2015 to 9/18/2015. Samples were collected using rectangular shape trays (31 cm × 17 cm) made of Teflon. The equipment was placed on the ground, close to the vegetables, and was under the effect of light, temperature and evaporation. At the end of each sampling period, and if there was no water, the trays were rinsed with 500 mL of distilled water, allowing to release sorbed particles and to produce a wet sample for analysis. Water samples were not filtered and the total concentrations were analyzed. In the case of metals and metalloids, samples were fixed by nitric acid addition prior to analysis.

2.2.2 Soil

Soil samples were collected in each UAG (Fig. 1) to characterize the main soil physico-chemical properties. Sampling included (1) disturbed soil samples representative of the 0–30 cm layer for textural characterization, organic matter, pH, carbonate content, cations, electrical conductivity, and macro and micronutrients. In each allotment, samples were collected in three locations, producing a composite sample; (2) undisturbed soil samples, collected in 282 cm³ metallic cylinders for determination of saturated soil hydraulic conductivity; (3) undisturbed samples, in 98 cm³ metallic cylinders for determining the water retention and bulk density. For (2) and (3), two replicates were collected at each site.

To evaluate the soil contamination, two soil samples were collected by allotment (at 0–5 cm and 20–30 cm), in January and June, totalizing 24 samples; each sample was the mix of a number of subsamples collected at the same depths in several points within the same area where dry and wet deposition samples were taken. Water and vegetables samples were taken also in this

vicinity. Soils were sampled using a Teflon or metal shovel and were properly identified and frozen for later analysis in the laboratory. Canadian legislation was used as reference, considering agriculture use and the values set for coarse and fine materials (Canadian Ministry of the Environment 2011).

2.2.3 Vadose Zone Water

To characterize the quality of interstitial water in the soil vadose zone, Teflon capsules were installed in PHG and LNEC allotments, at the depths of 30 and 60 cm for soil solution sampling. Samples were collected weekly during the winter (02/04/2015 to 05/13/2015) and the summer seasons (03/13/2015 to 08/21/2015), stored and preserved. A mixed sample for each period was analyzed. Again, the Canadian legislation was used for data comparison (Canadian Ministry of the Environment 2011).

2.2.4 Irrigation Water

Irrigation water samples were collected from three wells in two allotments (QG and LNEC) and analyzed for pH, electrical conductivity, nitrates, and heavy metals, using the same methodologies below described. In the other allotments, irrigation water was regular tap water provided by Lisbon's water supply and distribution company, and, as it is treated and daily analyzed, it does not present any contamination potential.

2.2.5 Vegetables

Plant samples were randomly collected from the various vegetable species being grown during the two sampling periods (January and June), corresponding to winter and summer seasons.

Although there was some diversity in the number of species planted in the different allotments, in order to better compare the results from the six different UAG, this paper focuses on the most common vegetables found, which were lettuce (*Lactuca sativa*) and cabbages (*Brassica oleracea*). These are also the most produced and consumed leaf vegetables in Portugal (INE 2016). The number of collected samples (one sample equals one vegetable) varied, but between two and six for each vegetable in each UAG. Each sample was analyzed in triplicate. In all cases, the vegetables were grown for domestic consumption. The most

frequent cropping system was a sequence of two or more crops a year.

2.3 Parameters Analyzed

A set of Polycyclic Aromatic Hydrocarbons (PAHs), metals and metalloids were analyzed in the samples collected. The 16 PAHs analyzed comprise acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, phenanthrene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, and pyrene. The 16 PAHs were analyzed in ten dry and wet deposition (five UAG and two periods); 24 soil samples (six UAG, two depths and two periods); and five vadose zone soil water samples (two UAG, two depths, different periods depending on water availability). The following metals and metalloids were analyzed: in ten dry and wet deposition samples—Ag, Al, As, B, Ba, Be, Co, Cr, Cu, Li, Mn, Ni, Pb, V, and Zn; in 24 soil samples—Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sb, Sr, Ta, Ti, V, and Zn; in seven vadose zone soil water samples (Al, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, Pb, Zn); and in 36 vegetables, collected in six UAG with a maximum of six vegetables each—Cd, Cr, Cu, Ni, Pb, and Zn. Finally, the following nutrients were analyzed for 24 soil samples and seven vadose zone soil water samples: NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} .

2.4 Methods of Analysis

In the laboratory, the water retention was measured in the sandbox apparatus (Stakman 1974) for pF between 0.4 and 2.0, and in the pressure plate (Richards and Fireman 1943) for pF 4.2. Saturated hydraulic conductivity was determined using the constant head method (Stolte 1997). The soil pH was determined by potentiometric methods. Organic matter was determined by dry combustion and infrared CO_2 quantification. Carbonates were determined by acid fumigation and infrared CO_2 quantification. The exchangeable cations were extracted with ammonium acetate and quantified by atomic absorption spectrophotometry (AAS). The exchangeable acidity was quantified by titration after extraction with KCl (Carter and Gregorich 2008). The macronutrients, including P_2O_5 , N-NO_3 and N-NH_4 were determined by molecular absorption spectrophotometry while K_2O was determined by flame photometry.

Micronutrients including Fe, Cu, Zn and Mn were extracted by the Lakanen-Ervio method and quantified by AAS.

For water and soil sample analysis, the US EPA 8270 and ISO 18287 were used for sample preparation and for determination of semi volatile organic compounds by gas chromatography method, with MS or MS/MS detection and calculation of semi volatile organic compounds sums from measured values. For metals and metalloids, US EPA 200.7, ISO 11885, US EPA 6010 were used to prepare samples and for the determination of elements by atomic emission spectrometry with inductively coupled plasma (ICP-AES) and stoichiometric calculations of compounds concentration from measured values including the calculation of total mineralization and calculating the sum of Ca+Mg. Samples were fixed by nitric acid addition prior to analysis. For metals, soil samples were homogenized and mineralized with *aqua regia* prior to analysis; for nutrients, the concentrations were measured in leach and recalculated for dry matter.

For vegetables, the species were identified, washed and stored for analysis. Samples (in triplicate) were oven-dried (60 °C) until constant weight. Dried sample were digested in concentrated nitric acid and the extracts were then analyzed by AAS (for Cu, Cd, Zn, Cr, Pb, and Ni), using flame or electrothermal atomization techniques depending on the level of metal in the extracts.

3 Results and Discussion

3.1 General Soil Properties

Table 1 presents the results of physical properties related to water transport and retention in the studied soils. The high moisture at saturation (θ_s) and low bulk density

(BD) values shown by the CHPL soils are associated with the high porosity resulting from the incorporation of large amounts of plant material. Soil water contents at field capacity (θ_{FC}) and wilting point (θ_{WP}) for QG and LNEC soils indicate higher retention capacity for water, with values of 220 and 200 mm of water per meter of soil depth, respectively. As for the permeability, PHG, LNEC, and QG soils present low values, while PHVC, CHPL, and CRIL soils are considered moderately conductive. Therefore, no significant leaching potential is expected. On the other hand, the less permeable soils present some potential for runoff losses and soil erosion with loss of the elements adsorbed to soil particles. The QG, PHVC, and LNEC soils present slightly higher contents of silt and clay, which may induce a potentially lower bioavailability of heavy metals than in the remaining soils.

As to the soil chemical properties, the results show that all of the UAG soils present alkaline reaction with the exception of CHPL which presents a neutral reaction. For these range of pH (alkaline and neutral), the bioavailability of heavy metals is low since they are preferentially adsorbed and/or precipitated (Thakur et al. 2016). From the plant perspective, the slightly alkaline pH values can be detrimental because they negatively influence the availability of certain macronutrients (P, K), micronutrients (Fe, Mn, B, Cu, and Zn) and the activity of microorganisms involved in fundamental processes, such as the nitrobacter responsible for nitrification.

Soils from CHPL and QG present high contents of organic matter (OM = 4.5%) resulting from the application of large amounts of organic composts and animal manure. These levels are favorable from the plant perspective since nutrients are retained in the OM cationic exchange sites in addition to sorption to fine clay particles (Baptista Neto et al. 2000; Moreno-Jiménez et al.

Table 1 Soil properties related to water transport and retention

UAG	Texture	θ_s ($\text{cm}^3 \text{cm}^{-3}$)	θ_{FC}	θ_{WP}	BD (g cm^{-3})	K_{sat} (cm d^{-1})
CHPL	Sandy loam	0.53	0.28	0.08	0.99	120
PHVC	Sandy clay loam	0.38	0.29	0.13	1.56	101
PHG	Sandy loam	0.43	0.30	0.13	1.46	54
QG	Loam	0.53	0.31	0.09	1.19	47
LNEC	Silty loam	0.45	0.28	0.09	1.40	72
CRIL	Sandy loam	0.37	0.27	0.11	1.45	90

2017). On the other hand, OM helps maintaining a soil structure adequate for the development of plant roots. From an environmental perspective, and for the same reason, the bioavailability of heavy metals will be low in these soils. LNEC, PHVC, and CRIL present low OM contents (1.2 to 2%) and a potentially higher heavy metal bioavailability.

3.2 Irrigation Water

The pH of the irrigation water used in the QG and LNEC allotments ranged between 7.5 and 8.0, which are normal values for the local waters. However, in two of the wells, one in each allotment, the electrical conductivity exceeded the maximum recommend potable water value of 1000 $\mu\text{S}/\text{m}$ (1340 $\mu\text{S}/\text{m}$ in QG and 1147 $\mu\text{S}/\text{m}$ in LNEC). Nitrates levels were below the maximum permissible value (50 mg/L) although in one of the wells at QG the value was close to this limit (47 mg/L). Heavy metals (Cu, Cd, Cr, Ni, Pb, and Zn) were also analyzed in the water from these three wells but the values were always below the acceptable limits for potable water.

3.3 PAHs Concentrations

Considering Lisbon city main pressures, a set of 16 PAHs was considered for analysis, using a harmonized sampling procedure and extraction and analyte quantification methods. PAHs are emitted to the atmosphere primarily from the incomplete combustion of organic matter (Abdel-Shafy and Mansour 2016). PAHs sources arise mainly from anthropogenic activities emissions (such as car and airplane emissions from combustion of fossil fuels, gas works, timber processing and treatment), although some PAHs arise from natural combustion (e.g., fires), petrogenic origin, and also some minor biogenic sources (from plants, algae/phytoplankton, and microorganisms) (Hursthouse 1996; Alloway 2004; Morillo et al. 2007; Leitão 2007; Folkesson et al. 2009; Mitchell et al. 2014; Hursthouse and Leitão 2016).

To measure the path of PAHs in the urban environment, and since PAHs are released into the atmosphere and distributed between vapor and particle phases, dry and wet deposition was analyzed. Furthermore, soil samples were analyzed to measure deposition and accumulation and vadose zone soil water to analyze leaching in the soil profile.

3.3.1 Dry and Wet Deposition

Figure 3 presents the results obtained for the PAHs concentrations in the dry and wet deposition. The concentrations of Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Fluoranthene, Indeno(1,2,3-c,d)pyrene, Naphthalene, and Pyrene were below the limit of quantification (0.01 mg kg^{-1} of dry weight). All these PAHs have high molecular weight, except naphthalene. LNEC, CHPL, and CRIL present more types of PAHs (with both high and low molecular weight) and in higher concentrations when compared to the other two UAG. In the latter, only acenaphthene occurred in PHVC.

Considering the city pressures, it is likely that the concentration ranges found in LNEC and CHPL are a result of their proximity to the airport and the airport plane corridor, while CRIL concentrations are related to the proximity to the major Lisbon traffic motorway. These deposition levels are about one order of magnitude lower than the ones found in other studies for European cities. Azimi et al. (2005) report values between 161 and 153 $\mu\text{g m}^{-2}\text{y}^{-1}$ for Paris and Créteil, respectively. Similarly, deposition fluxes of 365 $\mu\text{g}\cdot\text{m}^{-2}\text{y}^{-1}$ were observed in Texas (Lang et al. 2002). The lower values in Lisbon could be the result of the location of the city near the ocean, with high wind dispersion and mild temperatures along the year. The seasonal differences observed, with higher values in the colder period, were reported in other studies (Azimi et al. 2005) being attributed to residential heating, since vehicular traffic and industrial activities were considered steady along the year. In the case of Lisbon city, its mild climate results in comparatively few sources of household heating systems that potentially release PAHs to the environment, as most of these systems are electrically operated. On the other hand, the geographical location of the city, away from the main burned forest areas in the country, also reduces the possibility of accumulating PAHs due to forest fires. Conversely, the light and high temperatures for the June–September sampling period are likely to favor a rapid degradation of PAHs by photodegradation, which causes a greater fraction of the total PAHs to be in the vapor phase (Abdel-Shafy and Mansour 2016).

3.3.2 Soil and Vadose Zone Water

Figure 4 presents the results for the PAHs concentrations in the soils of the studied UAG, comprising two

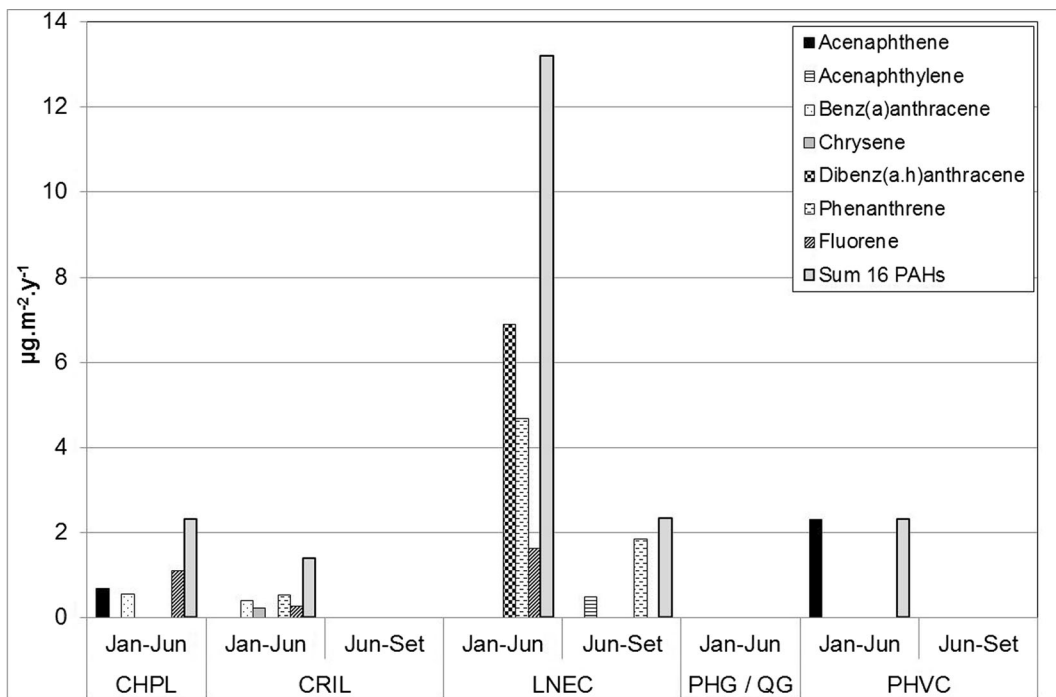


Fig. 3 Dry deposition PAHs concentrations in the six Lisbon UAG studied

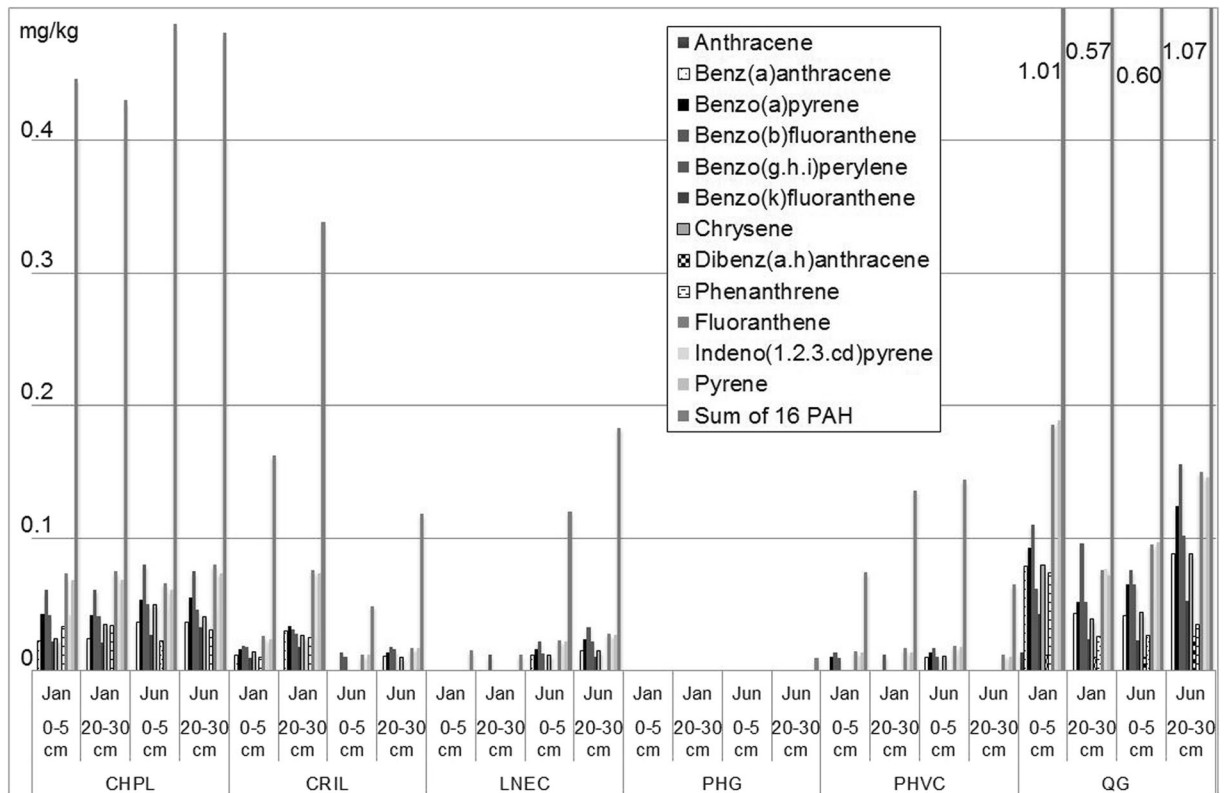


Fig. 4 Soil sample PAHs concentrations in the six Lisbon UAG studied

sampling periods, for the wet and dry seasons, and two depths (0–5 cm and 20–30 cm).

QG is the UAG where soil PAHs concentrations are higher, followed by CHPL, CRIL, and LNEC. The concentration ranges are lower than the values reported in similar studies conducted in European cities, e.g., 0.281–4.49 mg kg⁻¹ in Ljubljana, 0.148–3.41 mg kg⁻¹ in Torino, 1.49–51.8 mg kg⁻¹ in Glasgow (Morillo et al. 2007). Wilcke (2000) presents a summary of studies performed in 11 cities showing a range between detection limit up to 5.6 mg kg⁻¹, with calculated a mean of 4.42 and a median of 1.10 mg kg⁻¹. Considering the range of values proposed by the Canadian law (Canadian Ministry of the Environment 2011) for contamination of soils by PAHs, the studied soils only exceed the benzo(a)pyrene reference value for agricultural use (0.078 mg kg⁻¹) in the case of two samples from QG allotment where the values were 0.093 and 0.124 mg kg⁻¹.

PAHs concentrations in soils (QG > CHPL > CRIL > LNEC > PHVC > PHG) do not follow a similar pattern when compared to the dry deposition (LNEC > CHPL > CRIL > PHVC > PHG/QG). Besides, the low molecular weight PAHs found in atmospheric deposition (acenaphthene, acenaphilene, phenanthrene, and fluorene) are rare in the soil samples (only ten samples for phenanthrene and one sample of anthracene, a PAH not found in atmospheric deposition samples) and appear in lower concentrations than the high molecular weight PAHs, possibly due to their volatilization.

PHG, inaugurated in 2011, does not present hydrocarbons in any of the analyzed soil samples, but this can also result from the fact that the upper soils have been imported. The same applies to PHVC, a recent garden plot from 2013, but this one presents higher values in the first soil horizon. However, for QG UAG, which is located in the vicinity of PHG, the results obtained show the cumulative effect of the pressures in the soil concentrations. In fact, QG is the oldest UAG, with decades of accumulation of atmospheric deposition from a nearby road, and the gardening practices have helped incorporating that contamination and increasing the organic matter content (4.5% content: the highest together with CHPL), homogenizing the results in both depths. CHPL is a garden with direct pressure from the Lisbon airport air corridor. LNEC UAG, although close to the same air corridor, is not located exactly under it, and the gardens have started in May 2012. Also, the CRIL UAG can benefit from the positive effect of the presence of an

acoustic barrier, which reduces the contamination generated by CRIL road.

Concerning the two depths and two seasons analyzed, there is no clear pattern except for CRIL. In CRIL, the values in January are higher for both depths. One possible explanation for that is the use of runoff water of the Portela road (a small road parallel to CRIL) for irrigation in the wet season, contributing to the deterioration of its quality during this period. Apart from this exception, the dry season seems to have poorer conditions to dilute PAHs having, as a result, higher PAHs soil concentrations in some allotments (LNEC and QG). The data set show the migration capacity of hydrocarbons up to 30 cm in the soil, also a result from agriculture practices. However, no hydrocarbons were observed in the vadose zone soil water sampled in LNEC and PHG allotments. Soil seems to be the main sink for PAHs (Ockende et al. 2003; Morillo et al. 2007). This is probably due to the PAHs strong adsorption to the soil organic fraction (higher at CHPL and QG), together with the degradation of PAHs due to volatilization, in soils with lower permeability and biodegradation processes. As a result, PAHs have not been analyzed in vegetables since lower or null concentration is expected as uptake of PAHs by plants is small (Wilcke 2000).

Following the methodology presented in Morillo et al. (2007), the signature of sources was evaluated using molecular indices based on ratios of selected PAHs concentrations. These ratios use the fact that petrogenic contamination is characterized by the predominance of the lower molecular weight (LMW) PAHs (2 and 3 aromatic rings), while the higher molecular weight (HMW, 4 or more aromatic rings) PAHs dominate when the origin arises from combustion or pyrolytic processes such as fuel combustion in automobiles or airplanes (anthropogenic). The LMW: HMW ratio (the sum of the LMW concentrations divided by the sum of HMW PAHs concentration) has been used as an index to estimate the origin of the pollution. Values lower than 1 indicate anthropogenic origin. Besides, the following other ratios indicate that contamination by PAHs arises from anthropogenic sources rather than petrogenic origin (Morillo et al. 2007): PHE:AN < 10; FLT:PY > 1; INP:BPE < 1; BaA:CHR < 1; BbF:BkF > 1. The calculations made with the soil concentrations in the six UAG studied are presented in Table 2. The results confirm that the PAHs concentrations found in Lisbon city soils mainly derive from anthropogenic contribution.

Table 2 Molecular indices based on ratios of selected PAHs concentrations, according to Morillo et al. (2007)

UAG	Depth (cm)	Month	FLT + PY + PHE %	LMW:HMW	PHE:AN	FLT:PY	INP:BPE	BaA:CHR	BbF:BkF
CHPL	0–5	Jan	40.74	0.08	–	1.07	0.98	0.96	2.77
	20–30	Jan	40.27	0.08	–	1.09	0.98	0.69	2.90
	0–5	Jun	30.36	0.05	–	1.08	0.92	0.74	2.96
	20–30	Jun	35.71	0.06	–	1.08	1.00	0.90	2.27
CRIL	0–5	Jan	36.81	0.07	–	1.08	0.78	0.86	1.90
	20–30	Jan	47.55	0.07	–	1.03	0.89	1.11	1.72
	0–5	Jun	28.57	–	–	1.00	–	–	–
	20–30	Jun	20.51	–	–	1.00	0.88	1.10	–
LNEC	0–5	Jan	–	–	–	–	–	–	–
	20–30	Jan	–	–	–	–	–	–	–
	0–5	Jun	26.52	–	–	1.05	0.92	1.00	–
	20–30	Jun	22.73	–	–	1.04	1.05	1.00	3.00
PHG	0–5	Jan	–	–	–	–	–	–	–
	20–30	Jan	–	–	–	–	–	–	–
	0–5	Jun	–	–	–	–	–	–	–
	20–30	Jun	–	–	–	–	–	–	–
PHVC	0–5	Jan	25.68	–	–	1.07	1.00	–	–
	20–30	Jan	48.84	–	–	1.21	–	–	–
	0–5	Jun	24.32	–	–	1.06	1.00	0.91	–
	20–30	Jun	56.52	–	–	1.09	–	–	–
QG	0–5	Jan	44.46	0.10	5.29	0.98	1.10	0.99	2.56
	20–30	Jan	30.69	0.05	–	1.06	1.48	1.10	4.00
	0–5	Jun	36.56	0.05	–	0.98	0.85	0.95	3.30
	20–30	Jun	31.02	0.03	–	1.03	0.97	1.00	2.94

AN anthracene, BaA benzo(a)anthracene, BbF benzo(b)fluoranthene, BkF benzo(k)fluoranthene, BPE benzo(g,h,i)perylene, CHR chrysene, INP indeno(1,2,3-c,d)pyrene, FLT fluoranthene, PHE phenanthrene, PY pyrene, LMW sum of low molecular weight PAHs 2 and 3 aromatic rings, HMW sum of high molecular weight PAHs

3.4 Metals and Metalloids

3.4.1 Dry and Wet Deposition

Deposition of Al, Fe, and Mn is higher than all other heavy metals, mostly as a result of these three elements being the most abundant constituents of the lithosphere. The annual deposition values vary from site to site and show different seasonal behavior for winter and spring (January to June) and summer (June to September). The maximum Fe concentration was $341 \text{ mg m}^{-2} \text{ y}^{-1}$ at PHVC and for Al $287 \text{ mg m}^{-2} \text{ y}^{-1}$ at CRIL (Fig. 5). The sum of Al and Fe concentrations varies from 9.7 (LNEC) to $566.2 \text{ mg m}^{-2} \text{ y}^{-1}$ (CRIL). The maximum value is about two times the ones reported for bulk atmospheric deposition in Azimi

et al. (2005) for urban sites around Paris, where the sum of Fe and Al ranged from 258 to $291 \text{ mg m}^{-2} \text{ y}^{-1}$. This is probably due to the methodology chosen for collection of deposition, where the Teflon trays were placed on the soil, aiming to have a more exact measurement of the contaminants entering the soil, whereas atmospheric bulk deposition is typically taken at a height of 1.5 m above the ground. There is no clear pattern for winter/summer concentrations. These values compare to similar studies (Azimi et al. 2005).

Concerning the remaining heavy metals analyzed, their total concentration per UAG varies from 8.6 and $96.9 \text{ mg m}^{-2} \text{ y}^{-1}$ (Fig. 5). Previous studies have shown similar values for Paris with 28 to $131 \text{ mg m}^{-2} \text{ y}^{-1}$ (Guieu et al. 1997). Cd, Mo, Sb, Se, and Ta concentrations are below their

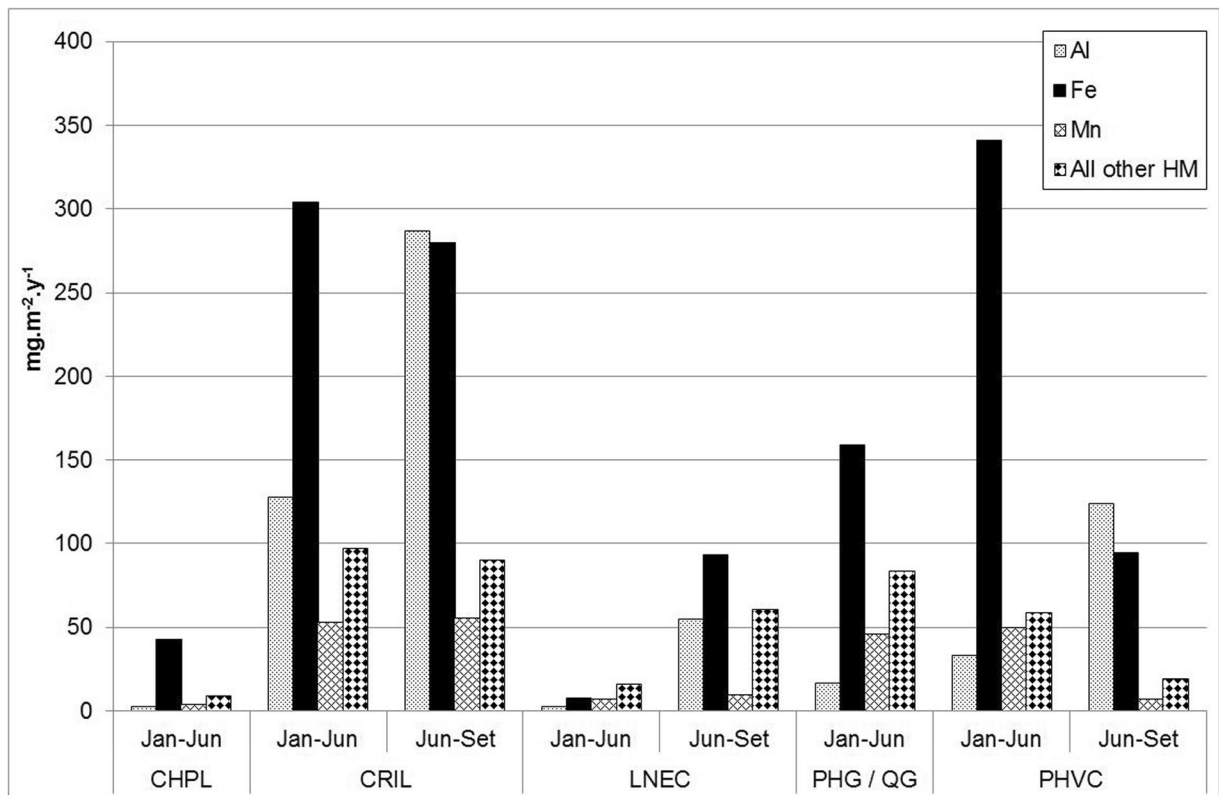


Fig. 5 Annual dry and wet deposition of Al, Fe, Mn, and the remaining total heavy metals analyzed in the six Lisbon UAG studied

quantification limit of 0.0004 (Cd), 0.002 (Mo) and 0.01 mg/L (Sb, Se and Ta), respectively. Table 3

presents some statistics for the concentrations of the remaining metals and metalloids in the dry and wet

Table 3 Mean, median, and range of metals and metalloids in the dry and wet deposition (mg m⁻² y⁻¹)

Metal	Mean	Median	Min	Max
Al	80.87	44.04	2.30	286.7
As	0.69	0.74	l.q.	0.86
B	10.07	6.18	l.q.	24.05
Ba	6.40	5.36	1.44	14.43
Be	0.03	0.03	l.q.	0.04
Co	0.48	0.45	l.q.	0.85
Cr	0.24	0.21	l.q.	0.66
Cu	1.24	1.18	0.13	3.98
Fe	165.19	126.80	7.42	341.0
Li	3.50	0.20	l.q.	10.20
Mn	28.91	27.73	3.45	55.52
Ni	0.70	0.24	l.q.	1.55
Pb	1.40	1.42	l.q.	2.10
V	0.60	0.28	l.q.	2.44
Zn	6.94	4.18	l.q.	18.76

l.q. limit of quantification

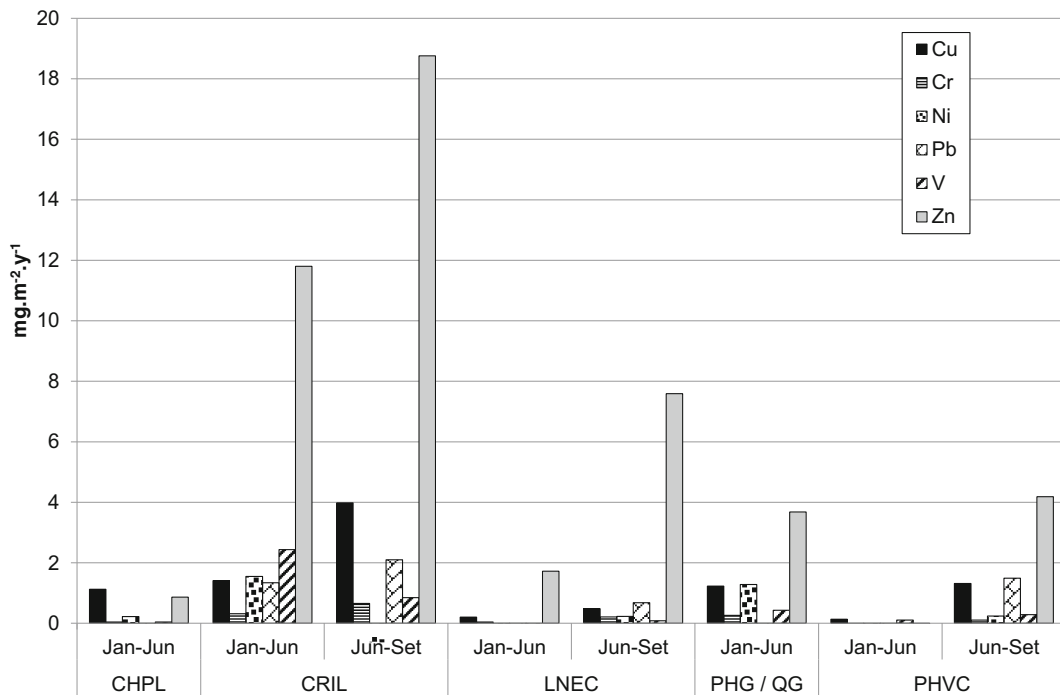


Fig. 6 Annual dry and wet deposition some heavy metals analyzed in the six Lisbon UAG studied

deposition and Fig. 6 the distribution of some of these metals in the different UAG and seasons.

Again, some seasonal differences can be seen but with no regular pattern among the UAG. Besides the most abundant metals (Al, Fe, and Mn), B, Zn, and Ba are identified as the following elements, with 32, 23, and 23%, respectively. These metals abundance has the order $B > Zn > Ba > Li > Pb > Cu > Ni > As > V > Co > Cr > Be$. The pattern found for dry and wet atmospheric deposition of PAHs, where the degree of contamination was $LNEC > CHPL > CRIL$ (Fig. 3), is no longer found for the metals and metalloids. It is likely that the presence of these elements in the deposited dust is attributed to road traffic sources, but also agriculture activity and the sites lithology which creates a dust richer in many of these elements.

3.4.2 Soil

Table 4 presents some statistics for the concentrations of the metals and metalloids found in the soil samples, and Fig. 7 the distribution of some of them for different depths and seasons. The soil concentrations for Hg, Cd, Ag and Ta were below their limit of quantification. These concentrations are within the range of the lower values found in previous studies done in several European cities

to assess metals spatial variability, including Lisbon (Imperato et al. 2003; Bechet et al. 2016).

Table 4 Mean, median and range of metals and metalloids in the soil samples (mg kg^{-1})

Metal/metalloid	Mean	Median	Min	Max
As	4.17	4.46	0.94	6.56
Ba	80.60	66.45	27.2	237.0
Be	0.85	0.87	0.44	1.18
Co	11.23	6.31	2.7	45.5
Cr	35.28	21.1	12.2	121.0
Cu	26.27	16.85	10.0	62.2
Li	19.42	19.1	11.4	27.4
Mn	247.64	154	62.7	994.0
Mo	0.57	0.6	<0.4	0.72
Ni	23.94	14.25	8.0	94.8
Pb	33.93	19.85	1.0	110.0
Sb	0.86	0.86	<0.5	1.02
Sr	65.09	25.75	12.4	282.0
Ti	2.78	2.1	<1	8.3
V	38.63	18.55	10.0	155.0
Zn	73.90	57.2	32.6	146.0
Fe	21,877	16,900	8880	63,500

UAG soils contain only a few elements whose concentration is above the reference threshold values used (Canadian Ministry of the Environment 2011). That was the case for several soil samples from CRIL (Co, with threshold 22 mg kg^{-1}) and Quinta da Granja (Pb, with threshold 45 mg kg^{-1}). Soils from CRIL present the highest concentrations for several metals: Fe, Mn, Ba, Sr, V, Cr, Ni e Co, partially due to their volcanic origin (Fig. 1), in agreement with the vanadium higher content, typical of these rocks. Exception to that are the concentrations in Zn, Cu, and Pb for which the higher values are found at Quinta da Granja (Fig. 7) and not at CRIL where these same heavy metals were higher in dry deposition (Fig. 6). This fact is attributed to the longer agriculture use of Quinta da Granja soil, with incorporation of the metals presented in road traffic, being consistent with the concentrations of PAHs (Fig. 4). In a similar way to what was found for PAHs concentrations, the concentrations observed in all soils for the different seasons or between the two depths analyzed is low, and this is probably due to the agriculture practices which mix these two depths. Similar behavior was found in other studies (Hursthouse et al. 2004). Concerning LNEC and CHPL UAG, the effect of the Lisbon airport is not clear in the soil metal content. The

concentrations can be a result of the background geochemistry, but exposure to traffic can also justify some of the concentrations obtained (Leitão et al. 2016). Considering the results for PAHs, this is likely to be the case for CRIL, LNEC, CHPL, and QG UAG. The current situation shows low concentrations, but a long term monitoring should be considered.

3.4.3 Vadose Zone Soil Water

The results obtained for the vadose zone water quality show that, with the exception of Ni, in all cases the values are compatible with reference values for potable groundwater (Fig. 8). This is probably due to the neutral to high pH, and clay and OM content, which favors trace elements adsorption and/or precipitation in the soil, and therefore low leaching capacities and availability for vegetables intake. No hydrocarbons were detected.

3.4.4 Vegetables

The concentrations of some of the metals analyzed for other environmental compartments were studied for the edible parts (leaves) of lettuce and cabbage. Although the roots were also analyzed, the results are not

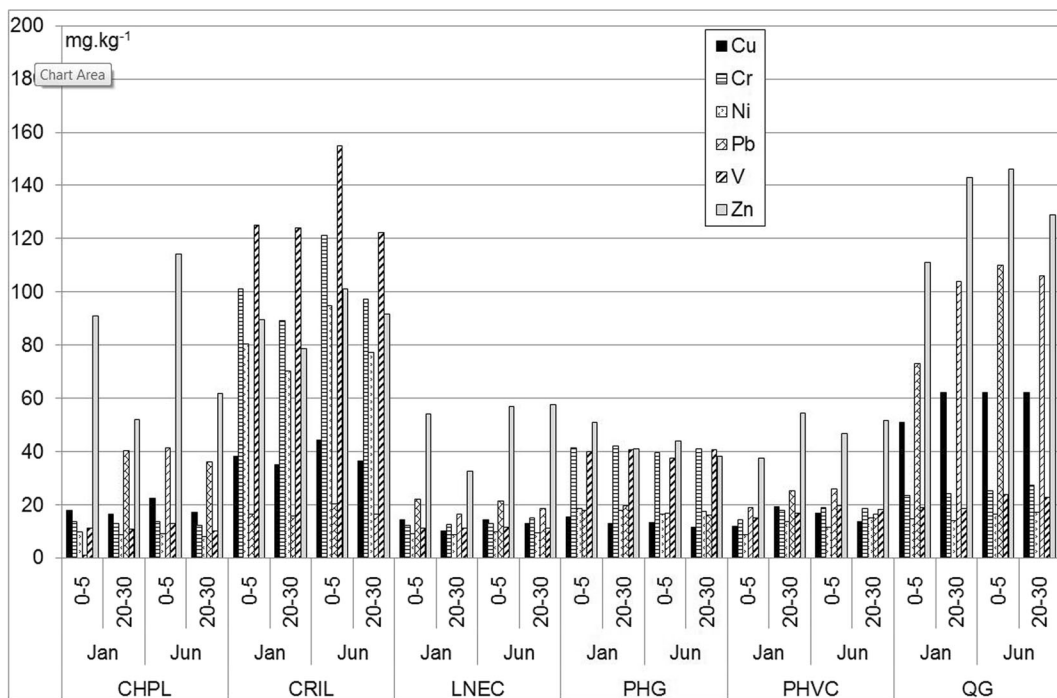


Fig. 7 Metals and metalloids distribution in the soil samples analyzed in the six Lisbon UAG studied

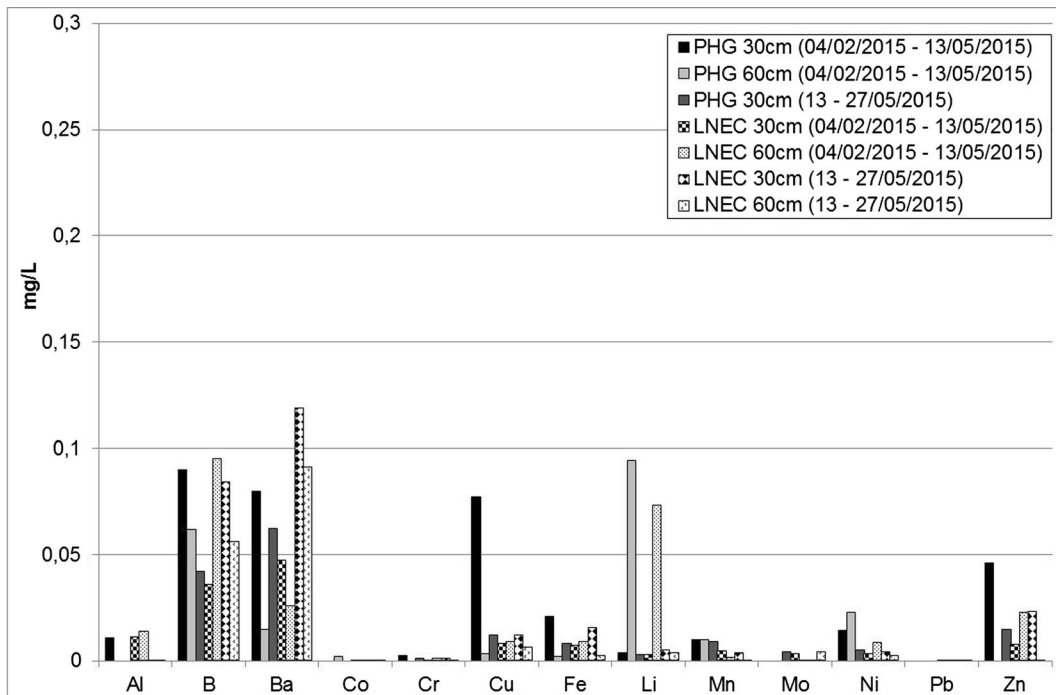


Fig. 8 Metals and metalloids concentrations in the vadose zone soil samples analyzed in the six Lisbon UAG studied

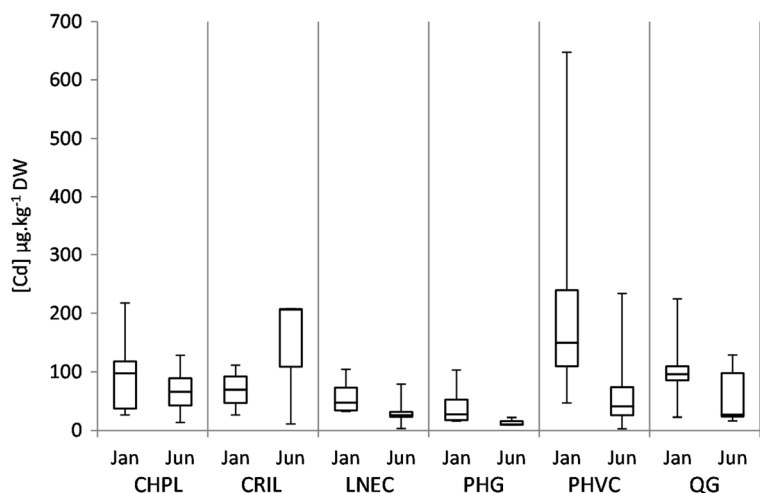
presented as these plant parts are not eaten and are left in the soil or immediately discarded.

The option for collecting lettuce and cabbage samples was due to the fact that these are, by far, the most popular vegetables grown in UAG in the Lisbon area and they are also plants very tolerant to different contaminants (Peijnenburg et al. 2000). Plants like lettuce are able to grow under high levels of contaminants, like heavy metals and still look healthy. This presents a

problem for the food chain contamination as they are not rejected by the potential consumer.

In Fig. 9 to Fig. 14, the results for the contents of Cd, Cr, Cu, Ni, Pb, and Zn are presented (in relation to dry weight, DW), as whisker plots containing all the collected data for lettuce and cabbage leaves, for each UAG and each sampling period (January or June). These two sampling periods correspond to a winter and a spring/summer season.

Fig. 9 Cadmium content in lettuce and cabbage samples in the six Lisbon UAG studied



Cadmium The Cd concentrations in leaves of lettuce and cabbage are presented in Fig. 9. Cadmium concentrations ranged between 2.8 and 647.5 $\mu\text{g kg}^{-1}$ DW, with a global average of 92.7 $\mu\text{g kg}^{-1}$. Generally, the average Cd levels in lettuce (146.3 $\mu\text{g kg}^{-1}$) were higher than in cabbage (53.6 $\mu\text{g kg}^{-1}$). There was a tendency for a decrease in the average Cd concentrations from the January sampling compared to the June one, and this was probably due to different atmospheric conditions, namely precipitation.

The maximum Cd levels in leaf vegetables, according to European regulations (Commission Regulation (EU) 488/2014 2014), are 200 $\mu\text{g kg}^{-1}$ fresh weight (FW). Considering that the average water content for the lettuce samples was 91.5% and for cabbage samples 84.9%, even the highest detected value for Cd (647.5 $\mu\text{g kg}^{-1}$ DW in a lettuce sample) corresponds to a considerably lower value, on a FW basis (56.9 $\mu\text{g kg}^{-1}$ FW), than the maximum legal limit.

Cadmium is a highly toxic metal, and so its presence in food products has to be carefully controlled (Clemens et al. 2013). This is especially important in vegetables, like lettuce, that are known to accumulate high levels of this element, as it is highly soluble in the soil solution and can easily be absorbed by plants. According to EFSA estimates, cereals and vegetables are among the main sources of Cd in human dietary exposure while vegetarians are exposed to roughly double the amount of Cd as non-vegetarians (EFSA 2009).

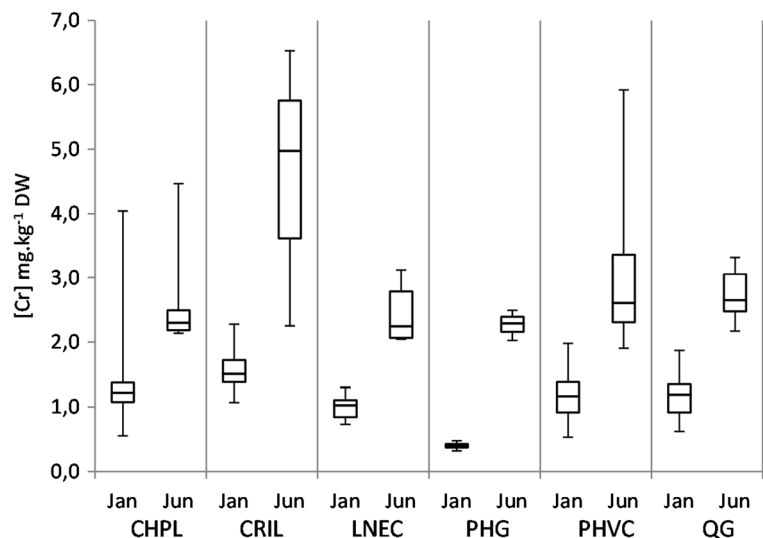
Cadmium levels in plants are highly variable, and dependent on soil contamination. In a study about

vegetables growing in contaminated sites in Uganda, the concentration of Cd in several edible vegetables ranged from 0.009 to 7.09 mg kg^{-1} DW (Nabulo et al. 2012), considerably higher than the ones obtained in the present study.

Chromium In Fig. 10, Cr concentrations in leaves of lettuce and cabbage are presented. The values ranged from 0.3 to 6.5 mg kg^{-1} DW. For Cr there was a clear increase in average Cr values in the June sampling, as observed for the dry deposition. Globally, as observed for the other metals, the average concentrations were higher in lettuce (2.5 mg kg^{-1}) than in cabbage (1.5 mg kg^{-1}).

Chromium can be present in nature in several states of oxidation being Cr(III) and Cr(VI) the more common, with the latter more toxic. Although Cr is essential for humans, it has not been shown to be so for plants. However, some studies have reported a stimulatory effect on plant growth with low concentrations of Cr (Zayed and Terry 2003). The normal levels of Cr in the soil range between 10 and 50 mg kg^{-1} , but can reach much higher values in ultramafic or contaminated soils, while in plants values between 0.006 and 18 mg kg^{-1} can be encountered (Shanker et al. 2005). As described above, the concentration of Cr in the soils of the UAG under analysis only exceeded 100 mg kg^{-1} in one allotment (CRIL, with ultramafic soils, cf. Fig. 7). It was also in this UAG that the highest concentration of Cr in a vegetable was detected (6.5 mg kg^{-1}) and the median value is highest compared to all the UAG. According to Zayed and

Fig. 10 Chromium content in lettuce and cabbage samples in the six Lisbon UAG studied



Terry (2003), typical values of Cr in plants growing in non-contaminated soils are usually lower than 1 mg kg^{-1} and rarely exceeding 5 mg kg^{-1} . The same authors also report that there is little correlation between Cr levels in soils and in plants, although in the present study the highest levels of Cr detected in soils also corresponds to the highest values in plants, but with a large variability in the results.

Chromium levels reported elsewhere are very variable. In a study of Hungarian urban gardens, the average Cr concentration in lettuce was 0.76 mg kg^{-1} (Szolnoki and Farsang 2013), while for white cabbage grown in the Berlin area a median of 0.48 mg kg^{-1} was reported (Säumel et al. 2012), both lower than in the present study. However, Nabulo et al. (2012) reported values between 1.34 and 65.2 mg kg^{-1} in different vegetables grown in Uganda and also concluded that there was no correlation between Cr in soil and in the studied plants.

Copper Copper concentrations in leaves of lettuce and cabbage are presented in Fig. 11. As Cu is an essential element for plants, the shaded area in the figure corresponds to the normal values found in plants. With the exception of an outlier (98.4 mg kg^{-1} DW in a cabbage sample from CRIL UAG) the normal values ranged from 0.41 to 18.15 mg kg^{-1}

DW. There was no systematic difference between the two sampling periods. Globally, the average concentrations were higher in lettuce (10.36 mg kg^{-1}) than in cabbage (7.23 mg kg^{-1}).

Copper is an essential micronutrient and the concentrations of this metal in plants are usually in the range of $5\text{--}20 \text{ mg kg}^{-1}$ DW in leaves (Yruela 2009). Copper concentrations under and above these limits might induce symptoms of deficiency or toxicity, respectively. Looking at the results presented in Fig. 11, it can be seen that, with the exception of one value, all the results are under 20 mg kg^{-1} , but several samples had values under 5 mg kg^{-1} . So, there was no case of contamination with Cu but in several instances the vegetables might be suffering from Cu deficiency. The outlier was probably due to a local contamination as it was a single sample from cabbage that presented such high values.

The values presented in Fig. 11 for plants confirm the results from Section 3.3 for soils as no soil sample exceeded 100 mg kg^{-1} and typical background concentrations of soils is usually reported to be between 2 and 50 mg kg^{-1} (Oorts 2013). The results from the present work are typical of the values found in similar studies from other urban areas. In urban gardens from Hungary, an average of 10.22 mg kg^{-1} DW was reported for lettuce

Fig. 11 Copper content in lettuce and cabbage samples in the six Lisbon UAG studied

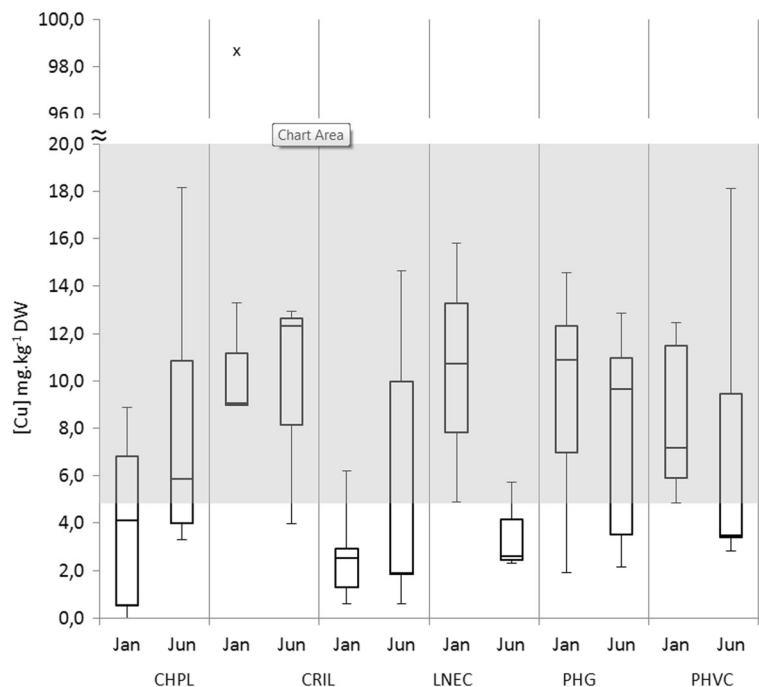
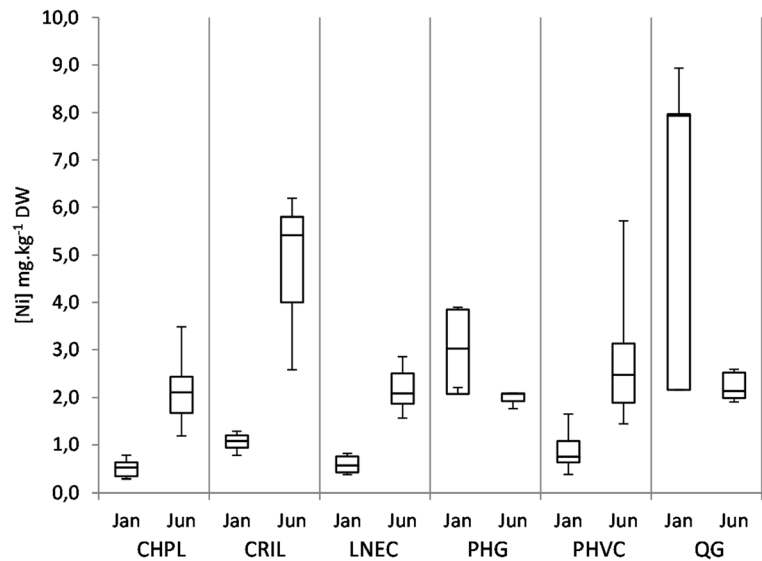


Fig. 12 Nickel content in lettuce and cabbage samples in the six Lisbon UAG studied



(Szolnoki and Farsang 2013) while the median for white cabbage samples in Berlin was 4.8 mg kg^{-1} (Säumel et al. 2012). Nabulo et al. (2012) reported values as high as 177 mg kg^{-1} DW, but in vegetables grown in contaminated areas in Uganda as in non-contaminated plots most of the concentrations found were below 20 mg kg^{-1} .

Nickel Nickel concentrations in leaves of lettuce and cabbage are presented in Fig. 12. The values ranged from 0.3 to 8.9 mg kg^{-1} DW. In most cases, there is a tendency of higher Ni concentrations in June when compared to January. Globally, the average concentrations were higher in lettuce (2.5 mg kg^{-1}) than in cabbage (1.8 mg kg^{-1}).

Nickel is a micronutrient essential for plants and for some microorganisms. It is generally considered that, for sensitive species, Ni is toxic at concentrations higher than 10 mg kg^{-1} while for more tolerant species this threshold can be as high as 50 mg kg^{-1} (Yusuf et al. 2011). The values obtained in the present study can thus be considered below toxic levels for plants. Thresholds for Ni toxicity for plants are difficult to establish since bioavailability is highly dependent on soil properties but is generally considered to be around 100 mg kg^{-1} (Gonnelli and Renella 2013). As the soils in this study had a maximum Ni concentration of 94.8 mg kg^{-1} (in CRIL UAG only) it is expected that the levels of Ni in the plants do not reach toxic levels, as observed. Reported values of Ni content in vegetables grown in urban gardens are usually within the range obtained in this work, in non-contaminated soils. In a study of urban

gardens in Hungary, the authors reported an average of 1.7 mg kg^{-1} DW in lettuce (Szolnoki and Farsang 2013), slightly lower than the values in the present work. Säumel et al. (2012) reported a median of 0.58 mg kg^{-1} in white cabbage collected in urban gardens in Berlin.

Lead The Pb concentrations in leaves of lettuce and cabbage are presented in Fig. 13. There were two outliers with concentrations of 5.46 and 7.45 mg kg^{-1} , both from the CHPL UAG (samples collected in June). As these two concentrations are way above the average from that same plot, it was probably due to some local contamination. Disregarding these two values, lead concentrations ranged between a 0.07 and 2.46 mg kg^{-1} , with a global average of 0.63 mg kg^{-1} DW. As observed for Cd, there is also a small decrease in the average Pb content between January and June. Like the results observed with Cd, the average content of Pb in lettuce (0.83 mg kg^{-1} DW) was higher than in cabbage (0.47 mg kg^{-1} DW).

According to European regulations (Commission Regulation (EU) 2015/1005 2015), Pb maximum levels in leaf vegetables is 0.3 mg kg^{-1} FW. Doing the same calculations as described for Cd regarding water content in the collected vegetables, it can be concluded that even the maximum value detected (for a lettuce sample) corresponds to 0.21 mg kg^{-1} FW, which is below the maximum level.

Lead is ubiquitous in cities, mainly due to anthropogenic activity, like the use of leaded gasoline for decades before a ban in this additive came in effect in the 80s and

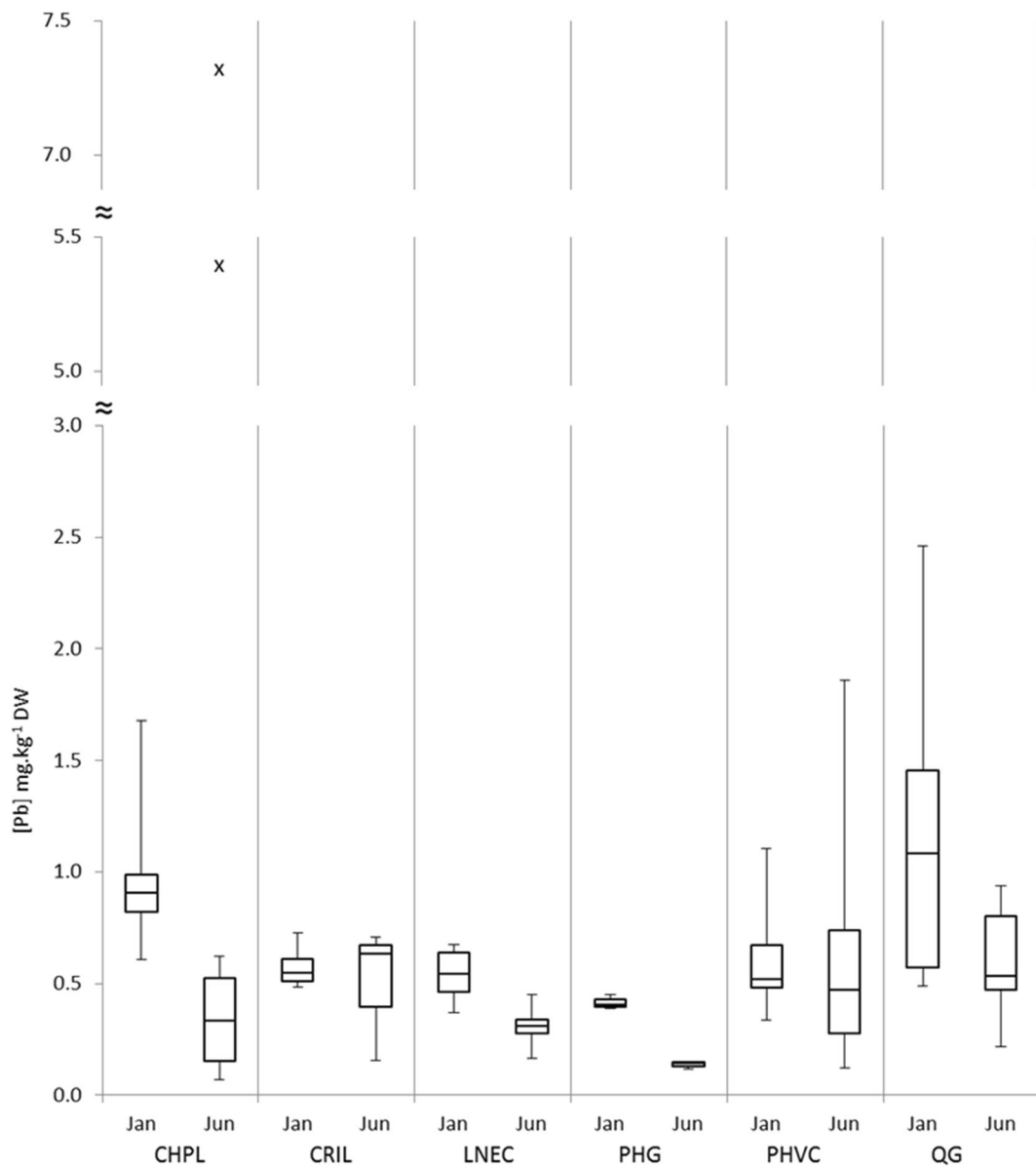


Fig. 13 Lead content in lettuce and cabbage samples in the six Lisbon UAG studied

90s. Although it's not very soluble in soil solution, it can be toxic to plants and animals at relatively low concentrations (Gupta et al. 2013; Nagajyoti et al. 2010). A long-term study of the presence of Pb in the Lisbon area has concluded that, since leaded gasoline was banned in Portugal in 1999, the levels of this heavy metal have been decreasing (Silva 2015). The present study confirms that, globally, the levels of Pb in lettuce and cabbage grown in the six UAG studied in this work are below the limits imposed by EFSA.

Lead values in vegetables grown in urban gardens are very variable and highly dependent on local pollution sources, present or past. For example, QG UAG, the oldest allotment studied, is the one where the Pb concentrations accumulated in soils are higher although no difference is observed in the air deposition. In a study about different vegetables grown in contaminated soils in urban areas in Uganda, Pb values in edible vegetables ranged between 0.143 and 144 mg kg⁻¹ DW (Nabulo et al. 2012). Like with Cd, these values are considerably

higher than the ones obtained in the present work, but that is expected as those soils were contaminated with heavy metals. The same authors also concluded that washing vegetables causes a large decrease in Pb content in plant parts (Nabulo et al. 2010). Moir and Thornton (1989) reported Pb values between 0.56 and 10 mg kg⁻¹ DW in cabbage and between <0.25 and 7.32 mg kg⁻¹ DW in urban gardens in the UK.

Zinc Zinc concentrations in leaves of lettuce and cabbage are presented in Fig. 14. As with Cu, Zn is an essential element for plants and the shaded area in the figure corresponds to the normal values found in plants. The values ranged from 16.1 to 104.3 mg kg⁻¹ DW. There was no systematic difference between the two sampling periods. Globally, the average concentrations were higher in lettuce (53.6 mg kg⁻¹) than in cabbage (28.7 mg kg⁻¹).

Zinc is usually present in plant leaves at concentrations of around 60 mg kg⁻¹ DW and toxicity due to excess Zn is not very common as plants are able to tolerate concentrations as high as 300 mg kg⁻¹ (Broadley et al. 2007; Mertens and Smolders 2013). The results presented in this work confirm that no toxic (or, for that matter, deficiency) amounts of Zn were detected in plants. Although some of the soil Zn values shown in Section 3.3 might be considered high, mainly for the QG UAG, this did not translate into toxic levels of this metal in the plants under study. The results presented in this work are in agreement with the reported values of lettuce

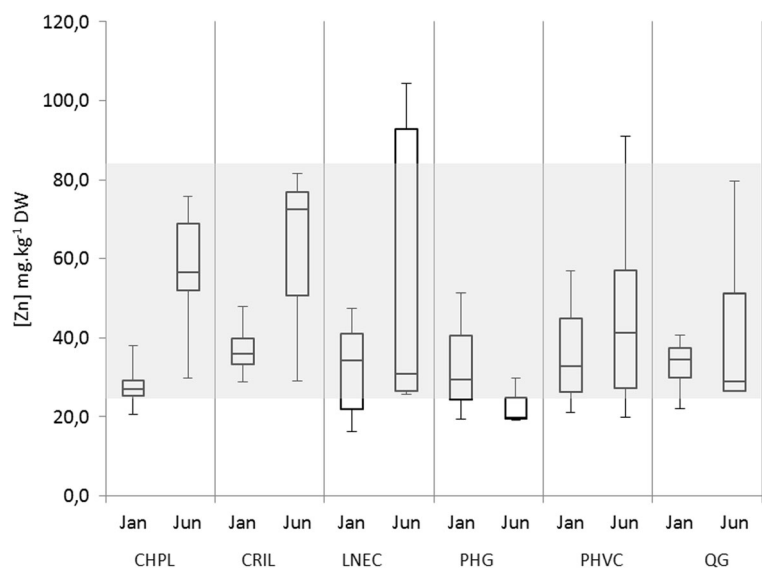
from Hungarian UAG, with an average of 38.75 mg kg⁻¹ (Szolnoki and Farsang 2013) and of white cabbage from Berlin allotments, with a median of 32.5 mg kg⁻¹ (Säumel et al. 2012). In fact, there is no known case of Zn poisoning in humans via the food chain, and at most, the toxic effects of the few cases of excess Zn manifest in plants and soil microorganisms (Mertens and Smolders 2013).

4 Conclusions

The environmental quality of six Lisbon city urban allotment gardens was assessed for the atmospheric deposition, soil, water and vegetables. The UAG covered soils with different lithologic origins, city pressures, and agriculture practices.

Dry and wet deposition measurements for PAHs reveal the impacts of the city pressures related to the airport plain corridor proximity (LNEC and CHPL) and to Lisbon major traffic motorway (CRIL). Nevertheless, levels are low and about one order of magnitude lower than the ones found in other European cities. UAG with higher PAHs in the total deposition do not relate to the ones with higher soil concentrations. The low molecular weight PAHs found in atmospheric deposition are rare in the soil samples. This is probably due to the PAHs strong adsorption to the soil organic fraction, together with the volatilization and biodegradation processes of

Fig. 14 Zinc content in lettuce and cabbage samples in the six Lisbon UAG studied



PAHs in soils with higher exposure to temperature and evaporation, and with lower permeability. The gardening practices seemed to have helped incorporating that contamination and homogenizing the concentrations in the two depths analyzed. The signature of sources evaluated using molecular indices based on ratios of selected PAHs concentrations indicated that contamination by PAHs arises from anthropogenic sources rather than petrogenic origin.

The presence of metals and metalloids in the dry and wet deposition is attributed to road traffic sources, but also the sites lithology. Strongest lithological contribution is observed in volcanic soils (CRIL and QG). UAG heterogeneity in metals concentrations is clearly a result of the background geochemistry, with the highest values belonging to the volcanic origin soils. Exposure to road and traffic deposition as well as airport can also justify some of the soil trace elements concentrations obtained, but there is not a clear effect from their influence.

The generally low levels of metals and metalloids in the soils are reflected in the values detected in the lettuce and cabbage samples. No significant contamination of these vegetables was detected in the studied UAG in both the winter and summer samplings.

Acknowledgements The authors would like to thank Lisbon Municipality, the EU COST office, LNEC, and research unit LEAF for their financial and practical support.

References

- Abdel-Shafy, H. I., & Mansour, M. S. M. (2016). A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25(1), 107–123.
- Alloway, B. J. (2004). Contamination of soils in domestic gardens and allotments: a brief overview. *Land Contamination & Reclamation*, 12(3), 179–187.
- Azimi, S., Rocher, V., Muller, M., Moilleron, R., & Thevenot, D. R. (2005). Sources, distribution and variability of hydrocarbons and metals in atmospheric deposition in an urban area (Paris, France). *Science of the Total Environment*, 337(1), 223–239.
- Baptista Neto, J. A., Smith, B. J., & McAllister, J. J. (2000). Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. *Environmental Pollution*, 109(1), 1–9.
- Bechet, B., Joimel, S., Jean-Soro, L., Hursthouse, A., Agboola, A., Leitão, T. E., et al. (2016). Spatial variability of trace elements in allotment gardens of four European cities: assessments at city, garden, and plot scale. *Journal of Soils and Sediments*, 1–16.
- Bell, S., Fox-Kämper, R., Keshavarz, N., Benson, M., Caputo, S., Noori, S., et al. (2016). *Urban Allotment Gardens in Europe*. Routledge.
- Broadley, M. R., White, P. J., Hammond, J. P., Zelko, I., & Lux, A. (2007). Zinc in plants. *New Phytologist*, 173(4), 677–702.
- Cameira, M. R., Tedesco, S., & Leitão, T. E. (2014). Water and nitrogen budgets under different production systems in Lisbon urban farming. *Biosystems Engineering*, 125(Supplement C), 65–79.
- Canadian Ministry of the Environment. (2011). Soil, Ground Water and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act.
- Carter, M. R., & Gregorich, E. G. (2008). *Soil Sampling and Methods of Analysis* (2nd ed.). Canadian Society of Soil Science. CRC Press.
- Clemens, S., Aarts, M. G. M., Thomine, S., & Verbruggen, N. (2013). Plant science: the key to preventing slow cadmium poisoning. *Trends in Plant Science*, 18(2), 92–99.
- Commission Regulation (EU) 488/2014 (2014). Amending Regulation (EC) No 1881/2006 as regards maximum levels of cadmium in foodstuffs. In O. J. L. 138/75 (Ed.).
- Commission Regulation (EU) 2015/1005 (2015). Amending Regulation (EC) No 1881/2006 as regards maximum levels of lead in certain foodstuffs. In O. J. L. 161/9 (Ed.).
- Cruz, N., Rodrigues, S. M., Coelho, C., Carvalho, L., Duarte, A. C., Pereira, E., et al. (2014). Urban agriculture in Portugal: availability of potentially toxic elements for plant uptake. *Applied Geochemistry*, 44, 27–37.
- Dunnett, N., & Qasim, M. (2000). Perceived benefits to human well-being of urban gardens. *HortTechnology*, 10(1), 40–45.
- EFSA. (2009). Scientific opinion of the panel on contaminants in the food chain on a request from the European Commission on cadmium in food. *The EFSA Journal*, 980, 1–139.
- Folkesson, L., Bækken, T., Brenčič, M., Dawson, A., François, D., Kuřimská, P., et al. (2009). Sources and fate of water contaminants in roads. In D. A. (Ed.), *Water in road structures. Geotechnical, geological and earthquake engineering* (Vol. 5). Dordrecht: Springer.
- Gonnelli, C., & Renella, G. (2013). Chromium and nickel. In B. J. Alloway (Ed.), *Heavy metals in soils: trace metals and metalloids in soils and their bioavailability* (pp. 313–333). Dordrecht: Springer Netherlands.
- Guieu, C., Chester, R., Nimmo, M., Martin, J. M., Guerzoni, S., Nicolas, E., et al. (1997). Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean. *Deep Sea Research Part II: Topical Studies in Oceanography*, 44(3), 655–674.
- Gupta, D. K., Huang, H. G., & Corpas, F. J. (2013). Lead tolerance in plants: strategies for phytoremediation. *Environmental Science and Pollution Research International*, 20(4), 2150–2161.
- Henriques, J. C. (2009). Urban agriculture and resilience in Lisbon: the role of the municipal government. *Urban Agriculture Magazine*, 22.
- Hough, R. L., Breward, N., Young, S. D., Crout, N. M. J., Tye, A. M., Moir, A. M., et al. (2004). Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations (vol 112, pg 215, 2004). *Environmental Health Perspectives*, 112(5), 215–221.

- Hursthouse, A. (1996). Environmental impact of the chemical industry. In A. Heaton (Ed.), *An introduction to industrial chemistry*. Dordrecht: Springer.
- Hursthouse, A., Tognarelli, D., Tucker, P., Marsan, F. A., Martini, C., Madrid, L., et al. (2004). Metal content of surface soils in parks and allotments from three European cities: initial pilot study results. *Land Contamination & Reclamation*, 12(3).
- Hursthouse, A. S., & Leitão, T. E. (2016). Environmental pressures on and the status of urban allotments. In S. Bell, R. Fox-Kämper, N. Keshavarz, M. Benson, S. Caputo, S. Noori, et al. (Eds.), *Urban Allotment Gardens in Europe* (pp. 142–164). Routledge.
- Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D., & Violante, P. (2003). Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environmental Pollution*, 124(2), 247–256.
- INE (2011). Censos 2011. http://censos.ine.pt/xportal/xmain?xpgid=censos2011_apresentacao&xpid=CENSOS. Accessed September 2017.
- INE (2016). Estatísticas Agrícolas 2015. Lisbon, Portugal.
- IPMA (2015). Normais Climatológicas. <https://www.ipma.pt/pt/oclima/normais.clima/>. Accessed September 2017.
- IWG, W. (2007). World reference base for soil resources 2006, first update 2007. Rome: FAO.
- Jean-Soro, L., Le Guern, C., Bechet, B., Lebeau, T., & Ringard, M.-F. (2015). Origin of trace elements in an urban garden in Nantes, France. [Journal article]. *Journal of Soils and Sediments*, 15(8), 1802–1812.
- Kabata-Pendias, A. (2001). *Trace elements in soils and plants* (4th ed.). CRC Press.
- Lang, Q., Zhang, Q., & Jaffe, R. (2002). Organic aerosols in the Miami area, USA: temporal variability of atmospheric particles and wet/dry deposition. *Chemosphere*, 47(4), 427–441.
- Leitão, T. E. (2007) Impact of road runoff in soil and groundwater. Portuguese and Other European case-studies. In *Water in Celtic Countries: Quantity, Quality and Climate Variability. Proceedings of the Fourth InterCeltic Colloquium on Hydrology and Management of Water Resources, Guimarães, Portugal* (pp. 338–347): IAHS Red Books, London.
- Leitão, T. E., Henriques, M. J., Cameira, M. R., Mourato, M., Rodrigo, I., Martins, M. L. L., et al. (2016). Evaluation of soil, groundwater and vegetable quality in Lisbon urban allotment gardens. Identification of mitigation measures aimed at protecting public health. Lisbon: Report 54/2016 – DHA/NRE, LNEC.
- Mata, D. D. A. (2014). The Lisbon's Green Plan Implementation. A Strong Tool Towards a New Urban Landscape. In *COST Action TU1201 - Urban Allotment Gardens in European Cities: Future, Challenges and Lessons Learned, LNEC, Lisbon, Portugal, March 2014*.
- Mata, D. D. A. (2017). Personal communication.
- McBride, M. B., Shaylor, H. A., Spliethoff, H. M., Mitchell, R. G., Marquez-Bravo, L. G., Ferenz, G. S., et al. (2014). Concentrations of lead, cadmium and barium in urban garden-grown vegetables: the impact of soil variables. *Environmental Pollution*, 194, 254–261.
- Mertens, J., & Smolders, E. (2013). Zinc. In B. J. Alloway (Ed.), *Heavy metals in soils: Trace metals and metalloids in soils and their bioavailability* (pp. 465–493). Dordrecht: Springer Netherlands.
- Mitchell, R. G., Spliethoff, H. M., Ribaud, L. N., Lopp, D. M., Shaylor, H. A., Marquez-Bravo, L. G., et al. (2014). Lead (Pb) and other metals in New York City community garden soils: factors influencing contaminant distributions. *Environmental Pollution*, 187, 162–169.
- Moir, A. M., & Thornton, I. (1989). Lead and cadmium in urban allotment and garden soils and vegetables in the United Kingdom. *Environmental Geochemistry and Health*, 11(3), 113–119.
- Moitinho de Almeida, F. (1986). *Carta Geológica do Concelho de Lisboa, Folha 1, 2 3 e 4, Escala 1:10 000*. Lisbon: Serviços Geológicos de Portugal.
- Moreno-Jiménez, E., Sepúlveda, R., Esteban, E., & Beesley, L. (2017). Efficiency of organic and mineral based amendments to reduce metal[loid]mobility and uptake (*Lolium perenne*) from a pyrite-waste contaminated soil. *Journal of Geochemical Exploration*, 174(Supplement C), 46–52.
- Morillo, E., Romero, A. S., Maqueda, C., Madrid, L., Ajmone-Marsan, F., Grcman, H., et al. (2007). Soil pollution by PAHs in urban soils: a comparison of three European cities. *Journal of Environmental Monitoring*, 9(9), 1001–1008.
- Nabulo, G., Black, C. R., Craigon, J., & Young, S. D. (2012). Does consumption of leafy vegetables grown in pen-urban agriculture pose a risk to human health? *Environmental Pollution*, 162, 389–398.
- Nabulo, G., Young, S. D., & Black, C. R. (2010). Assessing risk to human health from tropical leafy vegetables grown on contaminated urban soils. *Science of the Total Environment*, 408(22), 5338–5351.
- Nagajyoti, P., Lee, K., & Sreekanth, T. (2010). Heavy metals, occurrence and toxicity for plants: a review. *Environmental Chemistry Letters*, 8(3), 199–216.
- Ockende, W. A., Breivik, K., Meijer, S. N., Steinnes, E., Sweetman, A. J., & Jones, K. C. (2003). The global recycling of persistent organic pollutants is strongly retarded by soils. *Environmental Pollution*, 121(1), 75–80.
- Oorts, K. (2013). Copper. In B. J. Alloway (Ed.), *Heavy metals in soils: trace metals and metalloids in soils and their bioavailability* (pp. 367–394). Dordrecht: Springer Netherlands.
- Peijnenburg, W., Baerselman, R., de Groot, A., Jager, T., Leenders, D., Posthuma, L., et al. (2000). Quantification of metal bioavailability for lettuce (*Lactuca sativa* L.) in field soils. *Archives of Environmental Contamination and Toxicology*, 39(4), 420–430.
- Richards, L. A., & Fireman, M. (1943). Pressure-plate apparatus for measuring moisture sorption and transmission by soils. *Soil Science*, 56(6), 395–404.
- Sämel, I., Kotsyuk, I., Hölscher, M., Lenkerei, C., Weber, F., & Kowarik, I. (2012). How healthy is urban horticulture in high traffic areas? Trace metal concentrations in vegetable crops from plantings within inner city neighbourhoods in Berlin, Germany. *Environmental Pollution*, 165, 124–132.
- Shanker, A. K., Cervantes, C., Loza-Tavera, H., & Avudainayagam, S. (2005). Chromium toxicity in plants. *Environment International*, 31(5), 739–753.
- Silva, H. F. F. A. D. (2015). *Avaliação integrada da poluição por metais tóxicos na cidade de Lisboa*. Faculty of Sciences: University of Lisbon, Lisbon.

- Stakman, W. P. (1974). Measuring soil moisture. In: drainage principles and applications. Int. Inst. Ld. Reclam, 16(3), 221–251, Wageningen.
- Stolte, J. (1997). Determination of the saturated hydraulic conductivity using the Constant Head Method. In: J. Stolte (ed.), *Manual for Soil Physical Measurements. Technical document 37*: DLO Winand Staring Centre, Wageningen.
- Szolnoki, Z., & Farsang, A. (2013). Evaluation of metal mobility and bioaccessibility in soils of urban vegetable gardens using sequential extraction. *Water Air and Soil Pollution*, 224(10).
- Thakur, S., Singh, L., Wahid, Z. A., Siddiqui, M. F., At Naw, S. M., & Din, M. F. (2016). Plant-driven removal of heavy metals from soil: uptake, translocation, tolerance mechanism, challenges, and future perspectives. *Environmental Monitoring and Assessment*, 188(4), 206.
- Wilcke, W. (2000). Polycyclic aromatic hydrocarbons (PAHs) in soil—a review. *Journal of Plant Nutrition and Soil Science*, 163(3), 229–248.
- Yruela, I. (2009). Copper in plants: acquisition, transport and interactions. *Functional Plant Biology*, 36(5), 409–430.
- Yusuf, M., Fariduddin, Q., Hayat, S., & Ahmad, A. (2011). Nickel: an overview of uptake, essentiality and toxicity in plants. *Bulletin of Environmental Contamination and Toxicology*, 86(1), 1–17.
- Zayed, A. M., & Terry, N. (2003). Chromium in the environment: factors affecting biological remediation. *Plant and Soil*, 249(1), 139–156.