



Distribution of heavy metals and polycyclic aromatic hydrocarbons in holm oak plant–soil system evaluated along urbanization gradients



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HIGHLIGHTS

- Concentration ratios allow to evaluate the fate of pollutants in plant–soil systems.
- HMs and PAHs are subjected to a different fate in leaves and in soil.
- HM *Q. ilex* leaf concentrations mainly depend on root uptake and translocation.
- PAH *Q. ilex* leaf concentrations mainly depend on atmospheric depositions.
- High molecular weight PAHs are preferentially deposited on soil.

ARTICLE INFO

Article history:

Received 24 November 2014

Received in revised form 28 February 2015

Accepted 11 March 2015

Available online 27 April 2015

Handling Editor: Klaus Kümmerer

Keywords:

Organic and inorganic pollutants

Quercus ilex leaves

Topsoil

Bioavailable fractions

Bioaccumulation factors

ABSTRACT

Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) were analysed in topsoil and in *Quercus ilex* L. leaves from holm oak woodlands located along urbanization gradients (urban, periurban and extraurban sites) in two Italian regions (Campania and Tuscany). In each sampling site, the metal bioavailability factors (MBFs) and the pollutant bioaccumulation factors (BAFs) were calculated to estimate the fraction of each total metal concentration in soil potentially available to root uptake and to know the fate of both HMs and PAHs in the plant–soil system.

In general, the results indicated a low atmospheric deposition of pollutants and, in some cases, leaves and soils accumulated higher HM and PAH concentrations in the most urbanized areas. Correlation analyses showed that in each sampling site topsoil and leaves were exposed to the same atmospheric inputs of HMs and PAHs, although to a different extent. Notwithstanding the MBFs and BAFs differed between the two regions for the most HMs, they did not show a clear pattern in relation to the urbanization gradient. However, some information could be deduced by these ratios: the high BAF calculated for Mn shows that the foliar uptake plays an important role in accumulation of this metal. Moreover, for PAHs the different values of BAFs among low and high molecular weight compounds suggest their different fate, the first accumulated in leaves by stomata and the latter preferentially deposited on topsoil.

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1. Introduction

Heavy metal (HM) and polycyclic aromatic hydrocarbon (PAH) contamination poses a global environmental concern for ecosystems, often causing ecotoxicological effects (Fent, 2004).

Although the relative contribution of different sources to total HM emissions across Europe has changed in recent decades (van het Bolcher et al., 2006), metallurgical industries (foundries, smelters), heat and energy production, as well as railroad transportation, are among the main anthropogenic sources of airborne

Abbreviations: HM, heavy metal; PAH, polycyclic aromatic hydrocarbon; BAF, bioaccumulation factor; MBF, metal bioavailability factor; DTPA, diethylenetriamine-pentaacetic acid; TEA, triethanolamine; Ace, acenaphthene; Acy, acenaphthylene; Ant, anthracene; B[a]A, benz[a]anthracene; B[a]P, benzo[a]pyrene; B[b + k + j]F, benzo[b + k + j]fluoranthene; B[g,h,i]P, benzo[g,h,i]perylene; Crys, chrysene; DB[a,h]A, dibenz[a,h]anthracene; Flt, fluoranthene; Flu, fluorene; IP, indene[1,2,3-c,d]pyrene; Phen, phenanthrene; Pyr, pyrene; ANOVA, analysis of variance; MANOVA, multivariate analysis of variance.

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HMs; mining, municipal and industrial wastes and agricultural activities (wastewater irrigation, chemical fertilizers and pesticides) are sources of soil metal contamination (Panagos et al., 2013). HMs, with mineral oil, are the main contaminants, contributing around 60% to contamination in European soils (Panagos et al., 2013). High contents of HMs in soils would increase their potential uptake by plants, depending on the metal bioavailability which, in turn, is largely dependent on soil texture, pH, cation exchange capacity, moisture and organic matter content (Greger, 2004). The dynamics of HM uptake by plants from soil and their translocation have been recently modelled and the results have been experimentally validated (Guala et al., 2010 and references therein).

In the current scientific literature as a rule, to quantitatively characterise the transfer of a contaminant from soil to plant, the ratio of the contaminant concentration measured in vegetation to its concentration in the soil supporting that vegetation, is widely used (McKone and Maddalena, 2007; Kabata-Pendias, 2011). This approach assumes that, under equilibrium conditions, there is a relationship between the concentration of a certain element in the soil and that in the plant tissues. This assumption is well-grounded especially for non-essential and toxic HMs, whereas the content of essential elements is largely controlled by the plant metabolism. However, defining concentration in vegetation is often difficult, due to the different accumulation in different plant parts (roots, stems, leaves). For a summary of various definitions of the plant–soil bioaccumulation factors (BAFs), see McKone and Maddalena (2007).

PAHs are formed by the incomplete combustion or pyrolysis of organic materials. They can enter the soil, where contribute to about 10% of contamination (Panagos et al., 2013), through the atmospheric depositions and the fall of leaves or other plant parts containing PAHs. The litter decomposition, via fungal and bacterial metabolism and co-metabolism, can affect the total PAH concentrations in soil and their composition (De Nicola et al., 2014b). As a rule, the potential uptake of PAHs by plant roots is negligible due to their low water solubility and their adsorption to soil organic matter (Cornelissen et al., 2005) and/or clay minerals (Müller et al., 2007).

In terrestrial ecosystems, the tree canopies play an important role in the interception of atmospheric HM and PAH depositions, both in wet and dry forms. Morphological characteristics of leaves, such as the surface area and the presence of trichomes, may influence the adsorption of particulate HMs (Madejón et al., 2006), whereas cuticular waxes and lipophilic compounds favour the PAH uptake (Simonich and Hites, 1995). For both these classes of pollutants, downward fluxes to soil occur through the stemflow, throughfall and canopy drip processes (e.g. Horstmann and McLachlan, 1996; Xiao and McPherson, 2011).

Taking into account the results from our previous studies about the possibility of employ leaves and soil to assess inorganic and organic contamination and health hazard of urban areas, in this research we aimed at studying the fate of HMs and PAHs in holm oak plant–soil systems, in relation to different site typologies. To this purpose, we carried out this research in areas affected by different atmospheric pollutant loads in two regions (Campania and Tuscany; Italy), focusing on the distribution of HMs and PAHs in holm oak leaves and topsoils from woodlands along urbanization gradients. At this aim, the metal bioavailability factor (MBF) and the bioaccumulation factor (BAF) of HMs and PAHs were analysed in order to know the effective availability of metals and the fate of both the inorganic and organic pollutants in the plant–soil system. In addition, a correlation analysis was performed in order to point out possible common sources of pollutants. We focused our attention on *Quercus ilex* L. considering its suitability in biomonitoring of HMs and PAHs, yet demonstrated in our previous researches, its

ecological relevance as the climax species in most Mediterranean areas, and its resistance to several environmental stresses, which determines its broad use in urban afforestation.

2. Material and methods

2.1. Study area

The study was carried out in ten sites located in holm-oak woodlands along urbanization gradients of two Italian regions (Campania and Tuscany) characterised by a typical Mediterranean climate (<http://archivio-meteo.distile.it>). In both Campania (C) and Tuscany (T) regions, three sites were located in urban (U) areas, in order to take into account the higher variability of urban contamination in respect to that associated to periurban (P) and extraurban (E) woodlands, in which one site per typology was set up. In May 2009, at each site, four adjacent plots were randomly chosen and, at each plot, 5–6 holm oak trees were randomly selected. From the outer part of each canopy, at about 3–4 m above the ground, mature (one-year old) and healthy leaves were collected and successively pooled in a homogeneous sample for each plot. Under the canopy of the same holm oak trees, topsoil (0–5 cm) samples were collected with a plastic bucket after litter removing, and carefully mixed to obtain and analyse a homogeneous sample for each plot. In total, 40 samples of leaves and 40 samples of soil were analysed (1 leaf and soil sample per plot, for 4 plots, for 10 sites).

2.2. Chemical analyses

For total metal analyses, oven dried (75 °C until constant weight) soil and leaf samples were powdered in a planetary ball mill (Retsch, PM4) and, subsequently, 250 mg were mineralized in a microwave oven system (Milestone, Ethos) with the addition of 4 mL of 65% HNO₃ and 2 mL of 50% HF, to a final volume of 50 mL with bi-distilled water (see Baldantoni et al., 2009 for a full description). The available fraction of the same elements was extracted from 25 g of dried soil with 50 mL of a diethylenetriamine-pentaacetic acid and triethanolamine solution (0.005 M DTPA + 0.01 M CaCl₂ + 0.1 M TEA, pH 7.3) at room temperature in continuous agitation for 2 h, according to the official Italian methods for soil analysis (Violante, 2000). Total and available metal concentrations were measured in the sample solutions by atomic absorption spectrometry (PerkinElmer, AAnalyst 100) via graphite furnace (Cu, Ni and Pb) or flame (Fe, Mn and Zn). Standard reference materials (calcareous loam soil BCR CRM 141R and apple leaves NIST SRM 1515) were also analysed in order to assess the accuracy of the procedure for total metal determination in both soils and leaves. The percentage recovery of each element in standard reference material (ranging from 88% to 106% in soil and from 82% to 104% in leaves) was used to correct the quantification of the investigated metals. The precision of method, calculated as relative deviation standard ($n = 9$), ranged from 2% to 12%, depending on each element.

For PAHs analyses, fresh leaves (5 g) and air-dried soil (30 g) were added with anhydrous sodium sulphate and sonicated (Misonix, XL2020 sonicator) for three times, each in 100 mL of a mix dichloromethane:acetone (1:1 = v:v). The extracts were rotary evaporated to approximately 4 mL, filtered (PTFE filters 0.2 µm pore size), and dried under a gentle nitrogen stream. Consecutively, all the samples were resuspended with cyclohexane and analysed by GC–MS (HP 5890–HP 5971 with HP-5MS capillary column 30 m × 0.25 mm i.d. × 0.25 µm film thickness, for GC conditions see De Nicola et al., 2011). All analyses were performed in selected ion monitoring (SIM). Acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (B[a]A),

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