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Polycyclic Aromatic Hydrocarbons and Metals in Transplanted Lichen (*Pseudovernia furfuracea*) at Sites Adjacent to a Solid-waste Landfill in Central Italy

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Abstract The aim of the study was to evaluate the airborne contamination by polycyclic aromatic hydrocarbons (PAHs) and some heavy metals (arsenic [As], cadmium [Cd], chromium [Cr], copper [Cu], nickel [Ni], lead [Pb], and zinc [Zn]) of different pollution scenarios around a solid-waste landfill in central Italy using the lichen *Pseudovernia furfuracea* as a monitoring tool. For this purpose, eight stations around a landfill characterized by different air pollution sources (industrial, agricultural, residential areas, and roads with different traffic intensities), together with three stations far from the landfill (control areas), were monitored using a set of 22 lichen samples (11 samples analysed for PAHs and metals after 4 months, and 11 samples analysed for metals after 8 months). After 4 months of exposure, the lichen content of all of the analysed elements was greater than that in the pre-exposed lichens. In addition, the Cu and Pb concentration after 8 months was greater than the level after 4 months. The order of metal concentration was Zn > Pb > Cu (or Cu > Pb) > Cr > Ni > As > Cd in all cases. The range of $\sum$11PAHs concentration was 634–1,371 ng/g dw (three to seven times greater than the amount in the pre-exposed lichens). The $\sum$11PAHs were dominated (>70 %) by compounds with three aromatic rings. The comparison of the levels of air pollutants among the monitored stations shows nonrelevant spatial patterns between the landfill stations and the control areas; the levels of PAHs and metals found in the lichen samples around the landfill seemed to be more related to the general diffusion of these pollutants in that area.

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Landfills are the main option for nonhazardous or municipal solid-waste disposal in a great number of countries worldwide. The United States Environmental Protection Agency (USEPA) reported that more than half of the municipal solid waste produced in the United States was landfilled in 2010 (US EPA 2010), and the corresponding figure was, on average, 38 % in the 27 member states of European Union (Eurostat 2012). In the same year, the percentage of waste landfilled in Italy was greater than the overall European mean, corresponding to 51 % of the total waste treated (502 kg/capita) (Eurostat 2012).

Historically, the possible negative impact of landfills on the environment and human health has caused considerable concern for public health because of the presence of a large amount of contaminants at landfill sites. Despite the lack of strong scientific evidence of adverse health effects derived from exposure to landfill emissions (Porta et al. 2009), it is well known that the practice of disposing waste in landfills has inevitable consequences in terms of environmental pollution (El-Fadel et al. 1997). Indeed, municipal waste disposed into or onto landfills may contain several pollutants, such as heavy metals (e.g., mercury [Hg], lead [Pb],

chromium [Cr], and arsenic [As]), persistent organic pollutants, and polycyclic aromatic hydrocarbons (PAHs). Thus, landfills represent a permanent reservoir and a source of emission for several pollutants in environmental matrices (Chrysikou et al. 2008).

In addition, there is a common public perception that landfills present an unacceptable risk to human health and environments, and public risk perceptions often result in the NIMBY (not in my backyard), BANANA (build absolutely nothing anywhere near anything), LULU (locally unwanted land use), or NOTE (not over there either) responses, which are acronyms used for local objections to national projects on land use, including the siting of landfills (Wester-Herber 2004).

Given this scenario, it is vital to determine the impact of landfills on environmental matrices. Although extensive information regarding the emission of pollutants by way of landfill leachate and gas generation is available, data on air pollution related to landfills and its biological effects on adjacent environments are limited; in addition, there are no specific tracer compounds useful to monitoring air pollution around a landfill both because studies in this area are scarce and because the landfill emissions depend on the chemical composition of the treated waste (Koshy et al. 2009; Paoli et al. 2012). These types of data can be produced by routine environmental monitoring campaigns to evaluate both air quality and ecological impacts in support of regulatory procedures (Treweek 1999; Paoli et al. 2012). For this purpose, bioindicators, biomonitors and/or bioaccumulators, such as mosses, lichens, ferns, tree bark and higher plants, could be suitable tools. Indeed, botanical materials were used for biomonitoring of airborne contaminants, such as heavy metals, nitrogen oxides, ozone, PAHs, and dioxins/furans in different settings since 1950 (Guidotti et al. 2003; Augusto et al. 2007; Brunialti and Frati 2007; Nali et al. 2007; Baptista et al. 2008; Blasco et al. 2008; Guidotti et al. 2009; Augusto et al. 2010; Gjorgieva et al. 2011; Paoli et al. 2012; Špirić et al. 2013).

In particular, the advantages of lichens as biomonitors are intrinsic: they lack roots and consequently adsorb water and nutrients (as well as airborne contaminants) directly from the air. Lichens have be used as biomonitors and bioaccumulators both employing native species (Augusto et al. 2007; Blasco et al. 2008), which are species naturally present in the monitored area or by transplant techniques (Frati et al. 2005; Bergamaschi et al. 2007; Baptista et al. 2008; Sorbo et al. 2008), that consist in the use of thalli first removed from areas with no or little environmental contamination and then transplanted to the study area. The transplant techniques are used when lichens are scarce or absent in the study area (Frati et al. 2005; Sorbo et al. 2008; Augusto and Máguas 2013).

The accumulation of pollutants in lichens are influenced by the characteristics of pollutants (such as solubility, vapour pressure), the characteristics of lichen species, climate conditions (particularly temperature and rainfall), time of exposure of lichen to pollutants (Conti and Cecchetti 2001; Bergamaschi et al. 2007).

The aim of the present study was to evaluate the airborne contamination by PAHs and some heavy metals (As, cadmium [Cd], Cr, copper [Cu], nickel [Ni], Pb, and zinc [Zn]) of different pollution scenarios around a solid-waste landfill in central Italy using the lichen *Pseudovernia (P.) furfuracea* as a monitoring tool. For this purpose, the study was performed in an area surrounding a large landfill in the southeast of Rome (central Italy) characterised by different air pollution sources (industrial and agricultural activity, residential areas, and roads with different traffic intensities) and in three areas far from the landfill (control areas).

Material and Methods

Study Area

The investigated landfill (Discarica di Malagrotta 41°53′0″N 12°20′2″E) is situated west of Rome in the Latium region. According to some, the Malagrotta landfill is the largest waste discharge site in Europe; it extends over an area of 2.4 km^2, and every day it receives 4,500–5,000 tons of municipal waste.

A preliminary evaluation of the study area was used to select the locations for the monitoring campaigns. The sites were selected based on factors including the accessibility of the site, the presence of pre-existing supports (e.g., trees and wooden poles) for the positioning of lichen samples, and the occurrence of other emission sources of airborne contaminants. The Malagrotta area is characterised by different urban and industrial contexts: towns and residential areas, crops, farming and grazing regions, a refinery, gravel, fuel and gas storage facilities, and heavy traffic.

Table 1 Characteristics of the selected monitoring stations

Monitoring station	Type of area	Traffic density
Landfill		
St 1	Industrial area near a refinery	High
St 2	Parking area	High
St 3	Green area	Medium
St 4	Residential area	Medium
St 5	Residential area	Low
St 6	Residential area	Low
St 7	Rural area near a petting zoo	Low
St 8	Rural area	Low
Control		
St 9	Very urban area	High
St10	Urban area	Medium
St 11	Rural area	Low

In total, eight stations were selected around the landfill and near (40–50 m) different air pollution sources (stations [St] 1 through 8). Three additional monitoring St, sited at least 20 km far from the Malagrotta landfill, were selected in three residential areas at different traffic intensity levels and were used as control areas (St 9 through 11). We selected control points 9–11 far from the landfill area to evaluate the contribution of the traffic density to lichen bioaccumulation in areas located in the same province and, consequently, with similar climate conditions and other factors that could influence lichen bioaccumulation but without the influence of potential emission of pollutants from the landfill. The main characteristics of the monitoring stations are shown in Table 1.

Lichen Sampling

The monitoring campaign started in August 2008 with the collection of the epiphytic lichen *P. furfuracea* using the same modalities of withdrawal described in previous research (Guidotti et al. 2009). In brief, the lichen was collected in a remote area of Mount Terminillo (1,670 m [central Italy]) from the bark of beech trees at more than 1 m above ground level. The species *P. furfuracea* was chosen both for its wide distribution in the study area and for its ability to bioaccumulate PAHs and metals as shown in previous research (Guidotti et al. 2009). The transplant technique was used because of the absence of native lichens in some monitoring stations.

The entire sample was divided into 23 homogeneous subsamples of approximately 10 g each. Twenty-two subsamples were placed in separate bags of 20 × 20 cm; the bags were made of nylon net with a mesh size of 1 mm to prevent both the ingress of the macrofauna in the bags and the loss of piece of lichens. The subsamples prepared in this way were used for the biomonitoring of the 11 selected stations (2 subsamples for each station); the remaining subsample was immediately analysed to evaluate its content of metals and PAHs (serving as a blank).

Monitoring Campaign

Two sampling bags were suspended 2 m above ground level on a pre-existing support (tree or wooden pole) for each monitoring station. The monitoring campaign was performed from September 2008 to April 2009 for a total of 8 months. We chose this sampling period to perform the study under the typical winter conditions for three reasons: (1) in this period, the landfill operates at full load; (2) vehicular traffic is particularly intense; and (3) typical summer climate conditions in occidental countries can reduce the accumulation ability of lichen (Conti and Cecchetti 2001; Bergamaschi et al. 2007).

Two successive withdrawals were performed as follows: after 4 months, one of the two samples for each monitoring station was retrieved and taken to the laboratory for analytical determination of heavy metals and PAHs. After 4 additional months, the second sample was retrieved for each station, except for the sample at St 7, which was not found. All of the samples were taken to the laboratory for analytical determination of their metal content.

It is well known that in absence of specific time-studies for identifying the exposure period necessary to report significant results, the period of exposure of lichens to air pollution is chosen on the basis of the degree of pollution in the monitored areas and of the selected compound (Bergamaschi et al. 2007). In a previous study (Guidotti et al. 2009) performed with the same lichen species to monitor metals and PAHs, we found an accumulation rate of selected compounds $\geq$90 % for an exposure period of 3 months. Thus, we decided to prolong the exposure period of 1 month (retrieving the first set of transplanted lichen after 4 months) for assessing possible changes in accumulation of contaminants in *P. furfuracea*. In addition, we used a second set of transplanted lichen to evaluate the capacity of *P. furfuracea* to accumulate the selected metals until to 8 months of exposure.

Analytical Procedures

Subsample Pre-treatment

Each sample was kept at 40 °C for 48 h to permit dehydration. Subsequently, extraneous materials (dust, leaves, and chipping) were removed under a microscope. Each sample was then ground with an agate mortar.

Analytical Determination of Heavy Metals and PAHs

As, Ni, Cd, Pb, Cu, Cr, Zn, and PAHs (phenanthrene [phen], anthracene [anth], fluoranthene [flu], pyrene [pyr], benzo(a)antracene [B(a)A, chrysene [chry], benzo(b,k)fluoranthene [B(b,k)F], benzo(a)pyrene [B(a)Py], indeno(1,2,3cd)pyrene [IP], dibenzo(a,h)antracene [D(a,h)A], andbenzo(g,h,i)perylene [B(g,h,i)P]) were determined according to procedures outlined by Guidotti et al. (2009).

In brief, the analytical determination of metal content was performed using graphite-furnace atomic absorption spectrometry (AAS Varian Spectra AA 220Z, Varian, CA, USA). Before analysis, 150 mg of finely chopped lichen was placed into a ''Teflon bomb'' together with 7 ml of 63 % HNO_3, 3 ml of 30 % H_2O_2, and 0.2 ml of 40 % hydrofluoric acid (HF) and incubated in an oven at 120 °C for 3 h. The mixture was then transferred into a 50-ml glass flask together with bidistilled water. To eliminate the matrix effect, quantitative analyses were performed using the standard addition method. The replicability of the method was assessed by analysing a

Table 2 Certified and average recorded values for all metals according to BCR no. 482: Heavy metals in lichens, and average recovery rates (%), RSD, and LOQ for each compound

Metal	Certified value±uncertainty (μg/g dw)	Average recorded value (6 replicates) (μg/g dw)	Average recovery (%)	RSD (%)	LOQ (μg/g dw)
As	0.85 ± 0.07	0.84	98.8	16.7	0.02
Cd	0.56 ± 0.02	0.58	103.6	12.1	0.02
Cr	4.12 ± 0.15	4.61	111.9	9.8	0.03
Cu	7.03 ± 0.19	6.17	87.8	15.2	0.03
Ni	2.47 ± 0.07	2.44	98.8	11.0	0.03
Pb	40.9 ± 1.4	34.86	85.2	7.8	0.01
Zn	100.6 ± 2.2	100.4	99.8	11.1	0.02

reference standard material certified by the European Commission Community Bureau of Reference (BCR) (BCR No. 482 heavy metals in lichens) and repeating this procedure six times. The certified values, recorded values, average recovery, relative SD (RSD), and limits of quantification (LOQ) for each compound are reported in Table 1. Analytical determination of the PAH contents was performed using a gas-chromatograph mass spectrometer (GC-MS HP 6890 GC fitted with HP 5973 MS, Hewlett Packard, CA, USA) equipped with an HP5-MS column (25 m × 0.25 mm × 0.25 μm) (Hewlett Packard, CA, USA).

A total of 2 g of finely chopped lichen was placed into a 40-ml glass vial, and 30 ml of cyclohexane was added to the vial. The sample was extracted for 30 min at room temperature in an ultrasonic bath, and the final extract was filtered through filter paper to remove particles. The extraction was repeated with another 30 ml of cyclohexane, and the combined extracts were concentrated at 2 ml before purification. The final extract was concentrated to 1 ml using a Rotavapor system, and a total of 50 μl of internal standard (perylene d12 at 40 μg/ml in isooctane) was added.

GC-MS determinations were performed in the selected ion-monitoring mode. The linearity of the method was evaluated in the range of 5–500 μg/kg. The calibration curve showed an r^2 >0.99. The repeatability of the method was assessed by analysing six samples of lichen that had previously been extracted with the extraction mixture, supplemented at 100 μg/kg with a standard mixture (USEPA PAHs standard mixture at 2,000 μg/ml in methanol; Supelco, PA, USA). The average recovery rate (%), RSD, and LOQ are reported in Table 2.

The LOQ was defined as the concentration of the analyte that produces a signal-to-noise ratio of 9:1 and was determined for each PAH and metal using the calibration standard solution spiked at the lowest concentration level.

Data Analysis and Interpretation

The bioaccumulation of metals and PAHs in lichens was evaluated based on the exposed-to-control (EC) ratio introduced by Frati et al. (2005) and adopted in several studies (Bergamaschi et al. 2007; Sorbo et al. 2008; Guidotti et al. 2009). The EC ratio is calculated as the ratio between the level of an element in the lichen after its transplantation and subsequent exposure and the blank level. For the EC ratio calculation, when the blank value was less than the LOQ, the EC ratio was calculated by considering the blank to be equal to the LOQ. When the concentration of a compound after exposure was less than the LOQ, the EC ratio was not calculated. According to Frati et al. (2005), EC ratio values are interpreted based on the following criteria: severe loss-based EC = 0.00–0.25, somewhat loss-based EC = 0.25–0.75, normal EC = 0.75–1.25, accumulation EC = 1.25–1.75, and severe accumulation EC > 1.75.

The levels of each metal in the lichen samples were assessed on the basis of the scale suggested by Bargagli and Nimis (2002) and adopted by Paoli et al. (2012) to evaluate air pollution. The degree of air pollution in relation to the level of each metal (μg/g dw) was categorised as follows:

- Very low: As < 0.4, Cd < 0.3, Cr < 2, Cu < 9, Ni < 1.5, Pb < 10, Zn < 35
- Low: As ≤ 1.2, Cd ≤ 0.6, Cr ≤ 4, Cu ≤ 15, Ni ≤ 3, Pb ≤ 25, Zn ≤ 65
- Moderate: As ≤ 1.9, Cd ≤ 1.2, Cr ≤ 6, Cu ≤ 25, Ni ≤ 5, Pb ≤ 55, Zn ≤ 95
- High: As ≤ 2.5, Cd ≤ 2.1, Cr ≤ 13, Cu ≤ 40, Ni ≤ 7, Pb ≤ 95, Zn ≤ 135
- Very high: As > 2.5, Cd > 2.1, Cr > 13, Cu > 40, Ni > 7, Pb > 95, Zn > 135

Results and Discussion

Airborne Concentration of Metals

The EC ratios calculated for the metals (Fig. 1) demonstrate a great increase in the contents of all of the

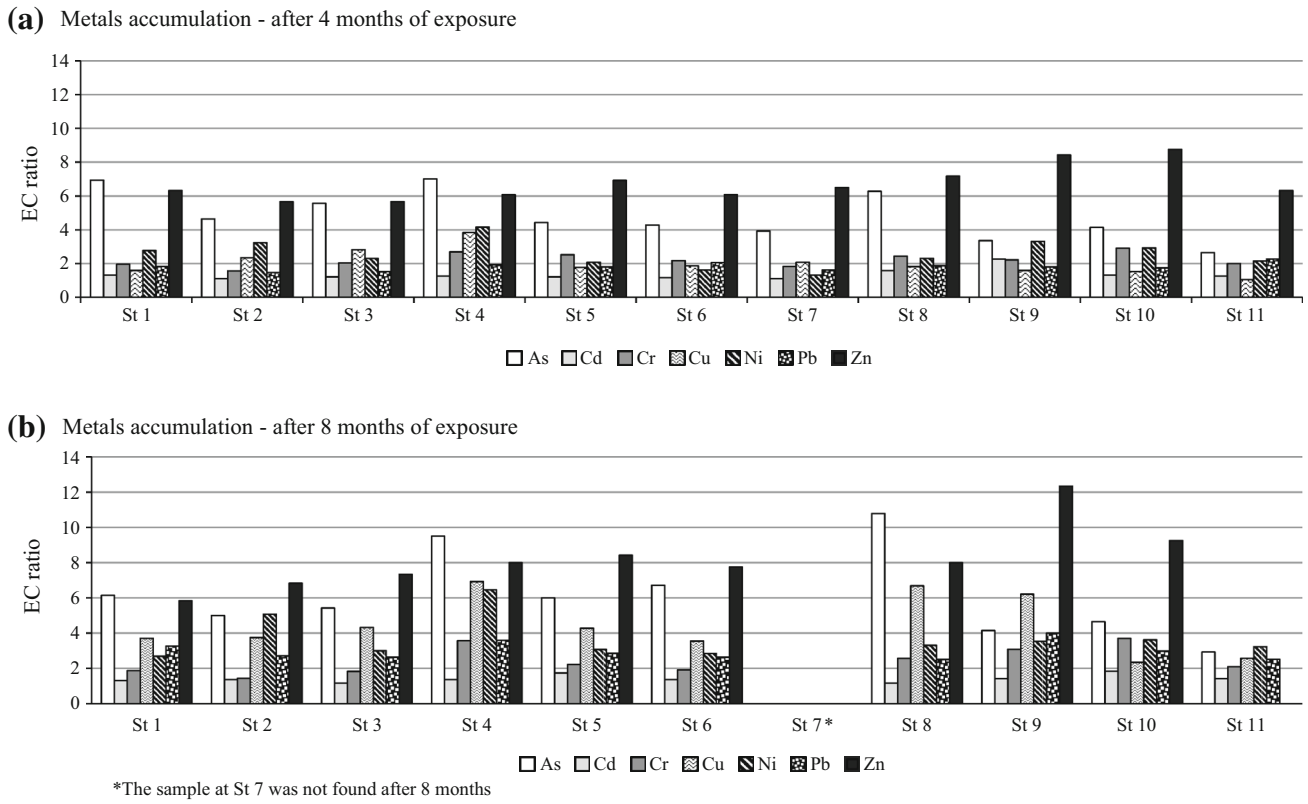

Fig. 1 Metal accumulation, expressed as an EC ratio, in lichen samples from each station after **a** 4 and **b** 8 months of exposure

elements in the exposed lichens compared with the pre-exposure content: 74 % of all of the data for each metal and location after 4 months of exposure showed EC ratios >1.75 (severe accumulation), whereas only 8 % of the values fell into the "normal" category (all of the samples for Cd and one sample for Cu). However, the EC ratios after 8 months of exposure fell into the normal category only for two samples (Cd in St 3 and St 8), whereas all of the other samples were classified as "accumulation" or "severe accumulation."

The average concentrations of the metals in the lichen samples before (blank) and after 4 and 8 months of exposure at each monitoring station are reported in Table 3. The order of metal concentrations was Zn > Pb > Cu (or Cu > Pb) > Cr > Ni > As > Cd in all of the samples after both 4 and 8 months of exposure. The same pattern was also found in the blank sample with the exception of As and Cd (Cd > As). These results are in line with previous Italian studies performed in different settings using several types of lichen species: forest ecosystems (Loppi and Pirintsos 2003); industrial, urban, and rural sites (Sorbo et al. 2008); and around a solid-waste landfill (Paoli et al. 2012).

Corresponding figures from other biomonitoring studies performed worldwide confirm that Zn commonly accounts for the most bioaccumulation, whereas the prevalence of the other investigated metals in lichen samples can be variable (Bajpai et al. 2011; Ng et al. 2005). Geographical differences in results have been attributed to differences in the industrial status of the studied countries, climatic, and environmental conditions that can affect the atmospheric transport and accumulation of metals in lichen samples (Ng et al. 2005) or differences in lichen species, which can accumulate metals in different ways (higher or lower ratios of accumulation) (Uluozlu et al. 2007). The similarity of our data to those reported in other Italian studies using

Table 3 Average recovery rates (%), RSD, and LOQ for each PAH

Compound	Recovery rate (%)	RSD (%)	LOQ (ng/g dw)
Phen	79	4.6	1
Anth	82	4.4	1
Flu	80	5.1	1
Pyr	77	5.6	1
B(a)A	82	4.1	1
Chyr	78	4.2	1
B(b,k)F	80	4.7	1
B(a)Py	77	3.9	1
IP	84	4.1	1
D(a,h)A	81	4.0	1
B(ghi)P	78	3.7	1

different lichen species shows that geographical differences are more likely related to differences in the urbanisation and climate characteristics of countries worldwide rather than the lichen species used for the biomonitoring studies.

The comparison of the concentration of each metal after 8 and 4 months of exposure indicates that, in many cases, the level of each element increased over time. Exceptions to these results include the following: As (Sts 1 and 3), Cd (Sts 3, 8 and 9), Cr (Sts 1 2, 3, 5, and 6), Ni (St 1), and Zn (St 1) as shown in Table 3. However, the amount of metal loss was <10 % for all of the elements except Cd (with losses ranging from 20 to 50 %). Increase and decrease in the metals concentrations in lichen during the period of exposure are described by other studies (Bari et al. 2001; Conti and Cecchetti 2001; Bergamaschi et al. 2007; Sorbo et al. 2008). Explanation to this phenomenon could be related to several factors known as determinants in the accumulation process of metals in lichen samples: differences in deposition and uptake of elements by lichen samples, differences in climate condition (especially related to temperature and rainfall), possible achievement of saturation stage, or a dynamic equilibrium between loss and accumulation. First, the deposition of the elements on lichens can occur through two different precipitation processes, namely normal or indirect precipitation. The indirect precipitation, which is achieved in highly stable atmospheric conditions, include mist, dew, dry sedimentation, and gaseous absorption and carry higher levels of nutrient and pollutants respect to normal precipitation (Conti and Cecchetti 2001). Thus, difference in atmospheric conditions could influence the process of deposition in lichen. As regard to the climatic conditions, it is well known that temperature and rainfall can impact on air pollution, on the deposition of elements on lichens, and on the vitality and metabolism of lichens (Bari et al. 2001; Conti and Cecchetti 2001; Bergamaschi et al. 2007; Sorbo et al. 2008). In this study, we exposed lichen samples for 8 months, thus avoiding the season with highest temperature (summer); however, we could not prevent the occurrence of rainfall with possible partial wash-out of elements deposited onto the lichen surface. Finally, it is possible that the accumulation of some elements in *P. furfuracea* reached a saturation stage or a dynamic equilibrium between loss and accumulation; it would be necessary to prolong the exposure period to confirm this hypothesis. Comparison of the levels of the metals according to the monitored stations did not show relevant spatial patterns between the stations surrounding the Malagrotta landfill and the control areas.

High levels for each metal after 4 months of exposure were recovered at St 4 for As, Cu, and Ni, at St 9 for Cd, at St 10 for Cr and Zn, and at St 11 for Pb. The highest concentrations after 8 months of exposure were found at St 8 for As, at St 10 for Cd and Cr, at St 4 for Cu and Ni, and at St 9 for Zn.

Airborne levels of metals expressed in terms of air pollution and evaluated based on criteria elaborated by Bargagli and Nimis (2002) are also presented in Table 3. All of the elements in the blank sample were found at concentrations indicative of very low air pollution, except Cr, which was at the level of low air pollution. In the exposed lichens, Cd was recovered at levels indicating low or very low air pollution at all of the monitoring stations, whereas the As, Cu, and Pb levels reached moderate air pollution. Cr, Ni, and Zn were found at different concentrations indicating air-pollution conditions from low to high or very high.

In our study, the highest concentrations in lichen samples were observed for Zn ranging from 68 to 105 μg/g dw and 70 to 148 μg/g dw after 4 and 8 months of exposure, respectively. Other recent Italian studies on heavy metal adsorption by *P. furfuracea* reported very different concentrations of Zn with mean Zn levels in urban environments of 24.6 μg/g dw (Sorbo et al. 2008) and 182 μg/g dw (Guidotti et al. 2009), and from 42.6 to 49.2 μg/g dw in 1996, 35.8 to 39.9 μg/g dw in 2000, 80.7 to 89.4 μg/g dw in 2008, and 41.2 to 52.2 μg/g dw in 2010 (Paoli et al. 2012).

Zn is a naturally and abundant occurring metal as indicated by its presence in the blank (12 μg/g); however, Zn can be released into environmental matrices from many types of anthropogenic sources, such as manufacturing and processing activities, incinerators, power plants, pesticides and fertilisers containing Zn, and traffic (Zn can be released from various vehicle components, such as tires and brakes) (Ng et al. 2005). Consequently, airborne Zn contamination can arise from various sources of these pollutants. In the present study, the major source of Zn in the monitoring stations located near roads with high traffic density (Sts 4, 9, and 10) was likely vehicular traffic as shown by the co-occurrence of high concentrations of metals traditionally related to traffic pollution, such as Cu, Cr, and Ni. In contrast, the major source of Zn in the monitoring stations located near roads with low traffic density (Sts 5 and 8) was most likely the use of pesticides and fertilisers for cultivation of farming fields (Scerbo et al. 2002).

Airborne Concentration of PAHs

The bioaccumulation of PAHs in lichen samples is shown in Fig. 2; it is remarkable that the EC ratio was >1.25 (accumulation or severe accumulation) for all of the compounds, except for B(a)Py and D(a,h)A, which showed

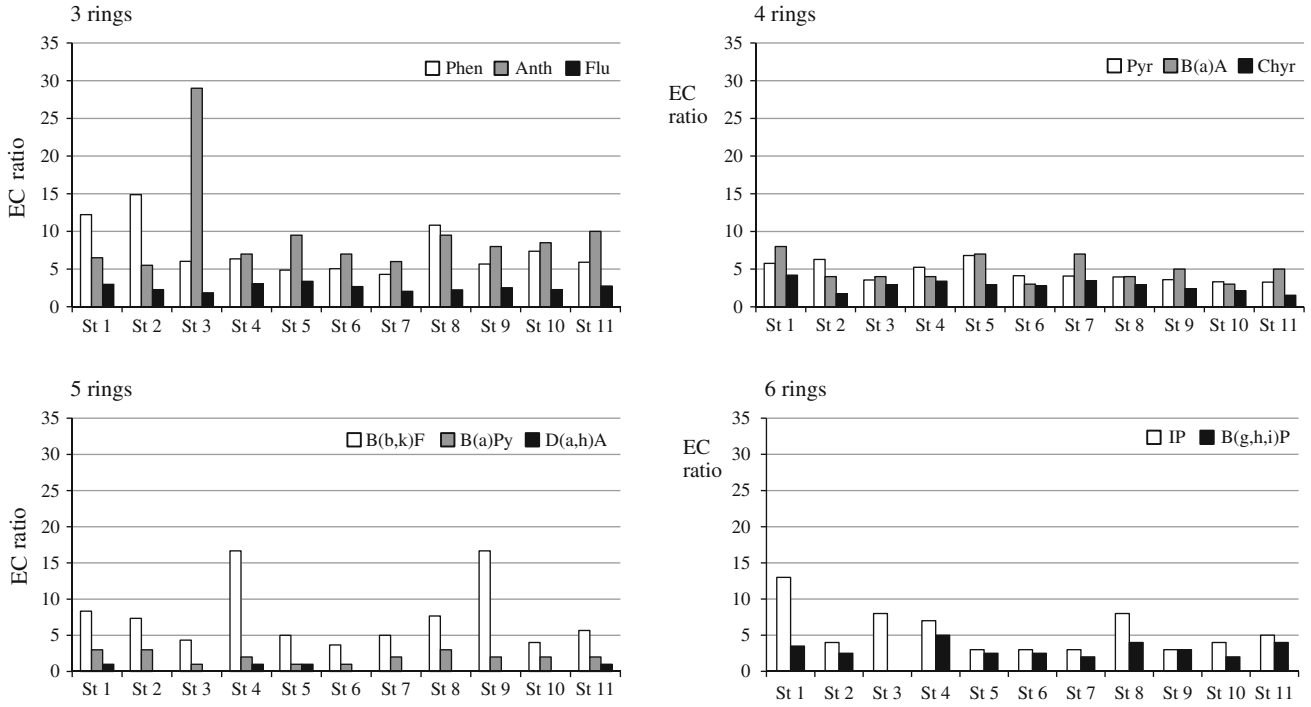

Fig. 2 PAH accumulation (according to the number of the aromatic rings), expressed as an EC ratio, in lichen samples at each station after 4 months of exposure

"normal" levels at Sts 3, 5, and 6 and at Sts 1, 4, 5, and 11, respectively.

The levels of each PAH found in lichen samples before and after 4 months of exposure are presented in Table 4. The ∑11PAHs concentrations ranged from 634 to 1,371 ng/g dw, i.e., from approximately three to seven times higher than the amount recovered in the blank sample Table 5.

A study performed on the native *Evernia prunastri* lichen, for example, reported total PAH concentrations from 638 to 5,031 ng/g dw (Blasco et al. 2008). Another study on the native *Parmotrema hypoleucinum* lichen found levels for a total of 16 PAHs that ranged from 95.5 to 73.8 ng/g dw (Augusto et al. 2010). The relevant differences in the levels of PAHs found in the present study with respect to previous findings can be attributed to several factors, such as different techniques of material collection (e.g., use of native or transplanted lichens), different lichen species used for the biomonitoring campaigns, and characteristics of the monitored areas, such as urbanisation, climate conditions, and air pollution levels.

Regarding the specific profile of PAH concentrations, the major contribution to the total amount of ∑11PAHs, which was >70 % in all of the monitoring stations, was composed of compounds with three aromatic rings (Phen, Anth, and Flu); the second-most dominant group of PAHs was composed of those with four aromatic rings (Pyr, B(a)A, and Chyr) followed by those with five (B(b,k)F, B(a)Py, and D(a,h)A) and six aromatic rings (IP, B(g,h,i)P).

These results are consistent with previous reports (Blasco et al. 2008; Shukla and Upreti 2009; Guidotti et al. 2009). It is remarkable that PAHs with three and four aromatic rings also contribute greatly to the total PAH load recovered at the monitoring stations near roads with low traffic density. This result can be explained by the fact that generally these PAHs are present in the gas phase in the atmosphere; thus, they are able to spread far from their emission sources (Yang et al. 1991). The low concentration of Anth in all of the monitoring stations can be attributed to its low thermodynamic stability (Zhou et al. 2005).

With regard to the comparison of ∑11PAH levels in the monitoring stations, concentrations of ∑11PAH at Sts 1, 2, and 8 are relatively higher than those measured at the other sites, but there were no relevant differences in the amount of PAHs between "landfill lichen samples" and "control areas lichen samples." In addition, it is remarkable that in all of the monitoring stations, the highest concentrations were identified for Phen, ranging from 279 to 967 ng/g dw, whereas the lowest levels were found for D(a,h)A (<LOQ in the majority of cases).

Table 4 Concentrations of heavy metals (μg/g dw) found in both unexposed (blank) and exposed *P. furfuracea* lichen at every sampling station after 4 and 8 months of exposure and air pollution grades[a]

Metal	Landfill								Control			Blank
	Industrial area HTDR St 1	Parking area HTDR St 2	Green area MTDR St 3	Residential area MTDR St 4	Residential area LTDR St 5	Residential area LTDR St 6	Rural area/ zoo LTDR St 7	Rural area LTDR St 8	Very urban area HTDR St 9	Urban area MTDR St 10	Rural area LTDR St 11	
After 4 months of exposure												
As	0.97**	0.65**	0.78**	0.98**	0.62**	0.60**	0.55**	0.88**	0.47**	0.58**	0.37*	0.14*
Cd	0.25*	0.21*	0.23*	0.24*	0.23*	0.22*	0.21*	0.30**	0.43**	0.25*	0.24*	0.19*
Cr	4.5***	3.6**	4.7***	6.2****	5.8***	5.0***	4.2***	5.6***	5.1***	6.7****	4.6***	2.3**
Cu	7.0*	10.3**	12.4**	16.9***	7.8*	8.2*	9.1**	8.0*	7.0*	6.7*	4.6*	4.4*
Ni	3.6***	4.2***	3.0***	5.4****	2.7**	2.1**	1.7**	3.0**	4.3***	3.8***	2.8**	1.3*
Pb	14.4**	11.6**	12.0**	15.3**	14.2**	16.2**	12.8**	14.8**	14.2**	13.8**	17.9**	7.9*
Zn	76***	68***	68***	73***	83***	73***	78***	86***	101****	105****	76***	12
After 8 months of exposure[b]												
As	0.86**	0.70**	0.76**	1.33***	0.84**	0.94**	-	1.51***	0.58**	0.65**	0.41**	-
Cd	0.25*	0.26*	0.22*	0.26*	0.33**	0.26*	-	0.22*	0.27*	0.35**	0.27*	-
Cr	4.3***	3.3**	4.2***	8.2****	5.1***	4.4***	-	5.9***	7.1****	8.5****	4.8***	-
Cu	16.3***	16.5***	19.0***	30.5***	18.8***	15.6***	-	29.4***	27.3***	10.3**	11.3**	-
Ni	3.5***	6.6****	3.9***	8.4*****	4.0***	3.7***	-	4.3***	4.6***	4.7***	4.2***	-
Pb	25.8***	21.5**	20.8**	28.4***	22.5**	20.8**	-	19.8**	31.6***	23.6**	19.9**	-
Zn	70***	82***	88***	96****	101****	93***		96****	148****	111****	95***	-

HTDR high traffic-density road, *MTDR* medium traffic-density road, *LTDR* low traffic-density road

[a] Air pollution grades according to Bargagli and Nimis (2002): * very low; **low; *** moderate; **** high; ***** very high

[b] Subsample of St 7 at 8 months was subtracted

Table 5 Concentrations of PAHs (ng/g dw) found in both unexposed (negative control–blank) and exposed *P. furfuracea* lichen at every sampling station after 4 months of exposure

PAH	Malagrotta								Control			Blank
	Industrial area HTDR St 1	Parking area HTDR St 2	Green area MTDR St 3	Residential area MTDR St 4	Residential area LTDR St 5	Residential area LTDR St 6	Rural area/ zoo LTDR St 7	Rural area LTDR St 8	Very urban area HTDR St 9	Urban area MTDR St 10	Rural area LTDR St 11	
Phen	795	967	392	413	316	328	279	704	368	479	384	65
Anth	13	11	58	14	19	14	12	19	16	17	20	2
Flu	229	175	143	236	260	206	158	173	195	175	212	77
Pyr	144	157	89	131	170	103	102	99	90	83	82	25
B(a)A	8	4	4	4	7	3	7	4	5	3	5	1
Chyr	63	26	44	51	44	42	52	44	36	32	23	15
B(b,k)F	25	22	13	50	15	11	15	23	50	12	17	3
B(a)Py	3	3	1	2	1	1	2	3	2	2	2	<LOQ[a]
IP	13	4	8	7	3	3	3	8	3	4	5	1
D(a,h)A	1	<LOQ[a]	<LOQ[a]	1	1	<LOQ[a]	<LOQ[a]	<LOQ[a]	<LOQ[a]	<LOQ[a]	1	<LOQ[a]
B(g,h,i)P	7	5	<LOQ[a]	10	5	5	4	8	6	4	8	2
$\sum$ PAHs	1,301	1,374	752	919	841	716	634	1,085	771	811	759	191

HTDR high traffic-density road, *MTDR* medium traffic-density road, *LTDR* low traffic-density road, *Phen* phenanthrene, *Anth* anthracene, *Flu* fluoranthene, *Pyr* Pyrene, *B(a)A* Benzo(a)antracene, *Chyr* Chrysene, *B(b,k)F* Benzo(b,k)fluoranthene, *B(a)Py* benzo(a)pyrene, *IP* indeno(1,2,3cd)pyrene, *D(a,h)A* dibenzo(a,h)antracene, *B(g,h,i)P* benzo(g,h,i)perylene

[a] Lower that the LOQ of the method

Conclusion

This study confirms the ability of *P. furfuracea* to accumulate PAHs and metals over time. In addition, the data obtained do not show relevant differences in air contamination for the monitored parameters between landfill and control areas; on the contrary, the levels of PAHs and metals found in the lichen samples around the landfill seem to be more related to the general diffusion of PAHs and metals in that area. Finally, according to a previous report (Paoli et al. 2012), the results of this study did not show a specific metal or PAH as a tracer for landfills.

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