Assessment of polycyclic aromatic hydrocarbons in industrial and urban areas using passive air samplers and leaves of *Tillandsia capillaris*

E.D. Wannaz *, G.A. Abril, J.H. Rodriguez, M.L. Pignata

Multidisciplinary Institute of Plant Biology, Section Pollution and Bioindicators, Faculty of Physical and Natural Sciences, National University of Córdoba, Av. Vélez Sársfield 1611, X5016CGA Córdoba, Argentina

A R T I C L E   I N F O

A B S T R A C T

This study extends the current knowledge regarding the use of passive air samplers (PAS) and biomonitoring with plants for the measurement of polycyclic aromatic hydrocarbons (PAHs), with the aim of evaluating the association between the accumulation of PAHs in leaves of *Tillandsia capillaris* and their concentrations in air measured by PAS. In addition, in order to study the seasonal variations of PAHs emitted by industries and vehicular traffic, a monitoring program was performed employing leaves of *T. capillaris* and polyurethane foam (PUF) disk passive air samplers. Results showed that both passive samplers and biomonitors presented the highest concentration values of PAHs in the dry season at sites with anthropic influence. Most of the PAHs were associated with urban and industrial sources present in the city of Córdoba. The concentration of ANT was associated with the presence of domestic sources; the use of natural gas as fuel for the cement plant was considered to be an important source of BaA and DBA enrichment was associated with vehicle emissions in this area. *T. capillaris* demonstrated to be a good accumulator of PAHs, considering that it reflected seasonal differences between different sites and that these were similar to those found in the passive samplers for the dry season. Therefore, these results contribute to the development of protocols for monitoring programs of PAHs that can be applied over large areas.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds containing two or more fused benzene rings formed by the incomplete combustion of organic matter [1–3].

Many of PAHs possessing mutagenic, carcinogenic and teratogenic effects are also distributed throughout the environment [4], with the Environmental Protection Agency (USEPA) having included 16 of these in the list of priority pollutants due to their mutagenic and carcinogenic properties [5]. PAHs can be found far from the source that produced them and in different environmental compartments such as air, water, soil and biota [6,7]. It is important to have access to data recording their presence and concentrations in the various regions of the globe, in order to be able to assess the potential risks to the environment and human health. In the atmosphere, PAHs may be present in the gas phase, adsorbed on aerosols, or partitioned between the two phases, depending on temperature, vapour pressure, solubility of the compound, and the size and surface area of the suspended particles

[8]. Deposition is an important path for PAHs leaving air and could be driven by gravity or washout of rain [9]. The dry deposition flux of gases and particles from the atmosphere to a receptor surface is governed by their concentrations in air, turbulent transport processes in the boundary layer, the chemical and physical nature of the depositing species, and by the efficiency of the surface to capture or absorb gases and particles [10].

Some of the techniques and tools used to obtain the concentrations of these contaminants in the air are expensive and require sophisticated equipment. Therefore an alternative is the use of passive air samplers (PAS) [11], which may be appropriate in remote areas or when the focus is on the "spatial mapping" of persistent organic compounds, given that they are cheaper, easier to handle and operate, and require no maintenance. Among the different strategies of PAS that have been developed are polyurethane foam disks (PUF), which have been used by several research groups worldwide [12–20] including to study a wide range of POPs (persistent organic pollutants) and semi-volatile organic compounds (SVOC) in the atmosphere. These include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OPs), polybrominated diphenyl ethers (PBDEs) and polychlorinated naphthalenes (PCNs) for indoor and outdoor studies. PUF disks have been shown to be capable of entrapping airborne particles

* Corresponding author. Tel.: +54 351 5353800x29771.
  E-mail addresses: ewannaz@com.uncor.edu, eduwannaz@gmail.com
(E.D. Wannaz).

[21]. The particle-phase sampling rate is expected to exhibit some variability among field sites depending on the total suspended particle concentration (TSP), the size distribution of particles, and various meteorological factors (e.g. wind speed, turbulence) [19,22]. The PUF disk is usually mounted on two stainless steel bowls for damping the flow of air within the disk and to protect it from light and precipitation. For persistent organic compounds (POPs), the PUF-air partition coefficient is similar to the octanol-air partition coefficient (K_{oa}), and the accumulation profile observes a linear phase, curvilinear phase and finally a steady state [23].

Another alternative to evaluate the quality of an environment is the use of plants as biomonitors of PAHs. It has been demonstrated that vegetation takes up semivolatile organic compounds such as PAHs, mostly from air, and the air quality can then be determined [24]. Biomonitoring of PAHs using plant leaves has been conducted in order to understand spatial distribution [25,26] and the impact of anthropogenic activities [27] as well as seasonal variations [28].

Currently the use of biomonitoring programs has been developed in several countries, being also mentioned in the European legislation [29]. This is because the use of biomonitors, in contrast to instrumental monitoring, provides results that reflect the total amount of pollutants and their interactions involved as well as their impact on living organisms. In addition, the use of biomonitoring programs allow to evaluate several sites simultaneously and cost is substantially lower than instrumental monitoring [30–32]. Among the plant species previously utilized for biomonitoring of PAHs, epiphytic species from the *Tillandsia* genus which are widespread in the Southern Hemisphere, have been showing to be suitable biomonitors for PAHs [33–35]. These species are common biomonitors used in studying heavy metals in the air due to their particular physiological characteristics [36–38]. The morphology of most species of *Tillandsia* consists of trichomes in the epidermal leaf surfaces, which allow the efficient absorption of scarce nutrients and liquid water directly from the atmosphere into the leaf [39]. Furthermore, a recent study from Papini et al. [40] on the ultrastructure of *Tillandsia* trichomes, described apoptotic mechanisms at maturity acting as a passive pump and thus achieving an important function in the absorption mechanism. *Tillandsia* genus is completely epiphytic, permitting a strong independence from the soil; thereby the only function of the adventitious roots is to adhere to a substratum. For this reason, it is especially suitable for air pollution monitoring, since the symptoms presented are clearly independent from soil conditions, thus making it easier to establish patterns for biomonitoring studies [41].

The objectives of this work were: (i) to study the seasonal variations of PAHs and their relationship to emission sources in different areas and (ii) to evaluate the association between the accumulation of PAHs in leaves of *Tillandsia capillaris* and their concentrations in air measured by PAS.

Materials and methods

Study area

The study was conducted at four sites in the province of Cordoba where there are different sources of air pollutant emissions (Fig. S1). These sites were (a) Center (CTR, 410 m.a.s.l.): center of the city of Córdoba, where the main source of pollutants is vehicular traffic, (b) Ferreyra (FER, 408 m.a.s.l.): neighborhood in the city of Cordoba where the main metal and mechanical industries of the province are located; (c) Yocsina (YOC, 580 m.a.s.l.): site with a cement industry that uses 75% gas and 25% alternative fuels in forms such as solid waste, and (d) Monte Cristo (MOC, 350 m.a.s.l.): a town located 25 km east of the city of Córdoba with approximately 10,000 inhabitants, where the main sources of emission in the study site are a company dedicated to the production of indoor and outdoor granite floors and also a firm dedicated to liquid fuel distribution. The weather conditions at the different sampling periods are presented in Table S1.

Periods of exposure

Two samplings were performed at different times of the year. The first study period began on March 21st and ended on June 21st, 2011, and the second study period began on September 1st and ended on December 1st, 2011. During these periods, adult specimens of *T. capillaris* and two passive air samplers were exposed at each site.

Polyurethane foam passive air sampler

At each sampling site, two passive sampler disks containing the polyurethane foam (PUF) were placed (Fig. 1). The PUF characteristics (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, and 0.01685 g cm^{-3} density) were similar to those described in previous investigations [13,42,43]. Before placing the PUF disk at the sampling sites, they were first washed with hot water and then with Milli Q water. Next, they were placed in soxhlet for 12 h with acetone and then with DCM for 12 h. The disks were dried in a desiccator, stored wrapped in foil and placed in glass bottles until used.

Biological material

Plants of *Tillandsia capillaris* Ruiz and Pav. *form capillaris* were collected from tree trunks at Intiyaco, Córdoba Province, Argentina (31°57'20'' S, 64°41'56.6'' W). This area is characterized by low emissions of air pollutants (considered to be an unpolluted site), where the baseline compositions of these plants have remained practically unchanged over the years. Net bags containing 8–10 plants were used to expose the biomonitors and were placed 3 m above ground level at the same high as PUF disks.

Extraction, cleanup and analysis of PAHs

Reagents and cleaning procedures

The solvents (DCM, hexane, acetone, acetonitrile) were of HPLC grade, and water was purified by a Milli-Q system (Millipore Corp.,

Fig. 1. Picture showing the passive air sampler and the bag with *T. capillaris*.

Bedford, MA). All glassware and plastic materials were washed using a commercial detergent, thoroughly rinsed with Milli-Q water and soaked for 24 h in acetone. From the assessment of blanks during testing and analysis, all indications showed that this method was very satisfactory (Table S2).

Standard solutions and Certified Reference Materials

Polycyclic aromatic hydrocarbon standard solutions (EPA 525 PAH Mix B) at 500 mg mL^{-1} were purchased from Supelco (Argentina). These contained: fluorene (FLU), acenaphthylene (ACE), phenanthrene (PHE), anthracene (ANT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo [a,h]anthracene (DBA), indeno[1,2,3-c,d]pyrene (IPY) and benzo[-g,h,i]perylene (BPE). Intermediate dilutions (500 ng mL^{-1}) were prepared weekly by an appropriate dilution of the stock solution in acetonitrile and water (6:4, v/v), and these solutions were used as calibrants following the external calibration method (0.2–50 ng mL^{-1}). Acenaphthylene was not measured because it has no fluorescence. Indeno[1,2,3-c,d]pyrene (IPY) was not measured since it elutes between dibenzo[a,h]anthracene (DBA) and benzo[g,h,i]perylene (BPE), and excitation and emission longitudes (290 and 430, respectively) are not good for a quantification of this compound.

The Certified Reference Material IAEA-140 OC (organochlorine compounds and petroleum hydrocarbons in seaweed), which contains the certified values for eight PAHs, was used to validate the method.

Table S2 reported PAHs recovery values after adding a known concentration and perform the PUF extraction and analysis. This table also shows the values of blank PUF for the two sampling periods and the detection limits was calculated as the mean blank value plus three times the standard deviation.

Analytical procedures

PUF disks were removed from the sampling sites after exposure, and the PAHs were extracted with ultrasound for 20 min twice using 350 mL of DCM at room temperature. Both portions were collected and then concentrated to a volume of 1 mL in a rotary evaporator. Subsequently, these were taken to dryness by evaporating the solvent with a stream of nitrogen. Finally, the samples were restored in acetonitrile (ACN) and water (0.5 mL; 6:4, v/v) for later analysis by HPLC.

The quantification of the PAHs in the samples of *T. capillaris* was performed according to the miniaturized method for the analysis of PAHs in leaf samples as described by Sanz-Landaluze et al. [44]. Before the PAHs were analyzed, fluorescence excitation and emission wavelengths were optimized in order to enhance the sensitivity and selectivity of the HPLC method (Table S3), with the column temperature being maintained at 28 °C during the chromatographic runs. The extraction procedure was performed by placing 300 mg of the homogenized material with n-hexane and acetone (2 mL; 1:1, v/v) in the extraction cell, which was then immersed in a water bath (0 °C) and exposed to ultrasonic irradiation for 30 s using an ultrasonic probe with a 3 mm titanium microtip (BioLogics, Inc.). The extracts were filtered with Sartorius filters (0.22 μm, Goettingen, Germany) and evaporated by a steady stream of nitrogen. Then, the residue was dissolved in acetonitrile (ACN) and water (0.4 mL; 6:4, v/v), and 25 μL of the reconstituted sample was injected into the liquid chromatographic column (Vydac 201TP C18, 250 mm × 2.1 mm; 5 mm, Deerfield, IL, USA) at a flow rate of 0.3 mL min^{-1}. The gradient elution program was started with an initial mobile phase at 60:40 (v/v) ACN:water, then changing linearly to 100% ACN at 18 min, and after a further 3 min changing back to the initial phase (60:40). The total run time for an analysis was 28 min. Identification of sample peaks was based on the retention times of standard substances, and qualitative and quantitative determinations were carried out using an HPLC Perkin Elmer Series 200 (Perkin Elmer, Norwaltk, CT, USA) equipped with a programmable fluorescence. To verify the reliability of the analytical procedure, a certified reference plant material (IAEA-140 OC) was measured repeatedly.

The recoveries ranged (Table S4) from 66% to 103% depending on the compound, with the lowest recovery values being for anthracene and benzo(k)fluoranthene. These had recoveries of 73 and 66%, respectively, which were similar to other results previously published [44–46].

Statistical analysis

The concentrations of PAHs at different study sites were submitted to an analysis of variance (ANOVA), and post hoc comparisons were made using the least significant difference (LSD) test, with a value of $p < 0.05$ being considered to be significant difference. A regression analysis was performed between the content of PAHs in the passive sampler and the content of PAHs in leaves of *T. capillaris*. A principal component analysis (PCA) was performed using the different sites as the classification criteria. The ratio of the concentrations of each PAH in exposed samples with that of basal samples (exposed-to-basal ratio, EB ratio) was used to calculate the accumulation rates in the *Tillandsia* leaves as in Frati et al. [47]. All statistical analysis was performed using Infostat software [48].

Results and discussion

PAHs in air

Table 1 shows the concentrations of PAHs found in the passive air sampling for the different sites in the two study periods, along with the sum of compounds with low molecular weights (LMW), those with three aromatic rings, and compounds with high molecular weights (HMW) which had four or more aromatic rings.

Regarding seasonal variations, these revealed that the concentrations of both LMW and HMW were higher in autumn (dry season) at all study sites. In addition, the sampling site with the highest concentration of PAHs was the industrial site (FER) for both sampling periods.

The fact that the highest concentrations of PAHs were found in fall may have been due to different weather conditions from this season compared to spring. For example, Table S1 shows that the average temperature in spring was higher than the average temperature in fall. Related to this, different studies have mentioned that the concentrations of PAHs in the atmosphere are higher in months with lower temperatures [49,50]. This may be because the PAHs are photo-sensitive and suffer a chemical degradation by irradiating sunlight. Several studies have identified photo degradation among the most important processes occurring in the atmosphere with respect to PAHs [51], with increased solar intensity resulting in an increased rate of photodegradation, leading to a lower concentration of PAHs in the atmosphere [8,51].

Differences in rainfall between the two periods might also have affected PAH concentrations in the atmosphere. It is known that scavenging of gas-phase PAHs in the atmosphere is thought to be proportional to K_{ow} [52], and Birgul et al. [53] showed a decrease in the total concentration (gas and particle) of PAHs in the atmosphere of Butal, Turkey with an increase of precipitation. In agreement, other authors such as Tham et al. [54] demonstrated a negative correlation between rainfall and the concentration of PAHs, indicating that the wash out effect of rain could be significant. These authors concluded that the meteorological conditions were predominant factors governing the seasonal

Table 1
Concentrations of PAHs at different sites obtained in passive air samplers.

PAHs (ng/sampler)	CTR Mean (n=2)	FER Mean (n=2)	YOC Mean (n=2)	MOC Mean (n=2)
	Dry season, 21st March–21st June			
FLU	1597.9 ± 148.6	1673.8 ± 368.2	1706.4 ± 402.8	411.1 ± 39.8
PHE	2160.3 ± 658.3	6279.3 ± 1158.8	5300.7 ± 2583.5	2674.6 ± 455.2
ANT	358.4 ± 26.8	39.1 ± 13.6	44.6 ± 6.8	0.7 ± 0.2
PYR	1390.1 ± 110.2	1687.3 ± 987.6	421.8 ± 127.3	196.4 ± 180.3
BaA	141.8 ± 95.6	108.7 ± 11.8	462.2 ± 56.3	109.8 ± 41.28
CHR	418.4 ± 163.2	408.6 ± 67.5	268.1 ± 36.4	161.6 ± 10.2
BbF	23.35 ± 3.52	25.30 ± 18.7	11.99 ± 2.35	13.07 ± 3.77
BkF	35.01 ± 10.0	30.44 ± 8.52	9.84 ± 5.62	12.25 ± 4.21
BaP	205.57 ± 52.35	192.27 ± 32.78	108.67 ± 21.88	70.93 ± 19.95
DBA	11.29 ± 6.52	4.81 ± 3.55	2.75 ± 1.34	39.73 ± 12.14
BPE	48.44 ± 13.11	124.13 ± 29.84	26.62 ± 3.84	0.29 ± 0.11
Σ LMW	4116.6	7992.2	7051.6	3086.4
Σ HMW	2273.9	2581.6	1312.1	604.0
Total PAHs	6390.5	10,573.7	8363.8	3690.4
	Rainy season, 1st September–1st December			
FLU	344.3 ± 50.5	1024.6 ± 189.9	232.4 ± 19.5	710.4 ± 352.2
PHE	2095.3 ± 352.8	5730.9 ± 1551.1	561.2 ± 69.6	1337.2 ± 411.1
ANT	375.3 ± 49.9	46.6 ± 3.98	32.15 ± 7.11	0.2 ± 0.13
PYR	544.9 ± 128.1	665.4 ± 456.3	221.0 ± 29.1	180.3 ± 48.6
BaA	99.2 ± 11.0	99.5 ± 13.5	125.8 ± 28.9	92.6 ± 36.2
CHR	190.3 ± 57.1	217.3 ± 20.0	76.6 ± 13.7	179.0 ± 41.1
BbF	21.87 ± 3.01	26.37 ± 3.02	2.73 ± 0.88	26.38 ± 3.87
BkF	17.79 ± 6.52	19.79 ± 5.30	11.49 ± 8.22	20.06 ± 6.20
BaP	54.91 ± 6.88	22.27 ± 4.01	29.24 ±	42.19 ± 6.77
DBA	10.39 ± 2.95	7.32 ± 1.68	0.21 ± 0.15	5.61 ± 1.11
BPE	39.18 ± 8.21	28.42 ± 4.55	12.62 ± 4.55	15.41 ± 4.88
Σ LMW	2814.9	6802.2	825.6	2047.8
Σ HMW	978.6	1079.2	479.8	561.5
Total PAHs	3793.5	7881.3	1305.4	2609.3

Σ LMW: sum of three-ring PAHs; Σ HMW: sum of four and five-ring PAHs.

variations of PAHs, but this study had the limitation that it was only carried out in the particle phase. In the present investigation, with regard to spatial differences the area with the highest concentrations of LMW and HMW was FER in the two sampling periods, an area which was characterized by the presence of metal and mechanical engineering industries and also by the presence of vehicle emissions.

Principal components analysis

In order to identify the PAHs associated with each study site, we performed a principal component analysis (PCA). This simplifies the interpretation of complex systems by transforming the original set of variables into a smaller set of linear combinations that account for most of the variance of the original set. The primary function of this analysis is the reduction of the number of variables, while still retaining as much of the original information as possible. Variables with similar characteristics are grouped into factors, which can be interpreted either as an emission source or as a chemical interaction [55].

The PCA was applied to the correlation matrix instead of the covariance matrix to avoid the scale effects of the variables involved [48]. Our analysis was undertaken using the different sites as the classification criteria, with the eigenvalues corresponding to the first three components being displayed in Table 2 and the results presented in biplots (Fig. 2). These results showed that most of the PAHs quantified in the PAS in this study (FLU, BPE, PYR, CHR, BaP, BkF y BbF) contributed to the first component, which could indicate a common emission source for these compounds. The variables that contributed most to the second component, DBA and BaA (BaA was negative), which may indicate that two different sources contributed to this component, and the last component was marked by variable ANT.

Fig. 2 shows the graphs of the various components and it can be observed that the first component was associated with the FER and CTR sites, which might indicate both mobile and industrial sources. This is in agreement with a previous research study that observed that PAHs markers for mobile sources are mainly of low molecular weight, as for example: ACE, fluranthene and FLU [56]. Harrison et al. [57] reported that BbF, BPE and PYR are markers for diesel-powered vehicles, and BPE was identified as a typical tracer of vehicular sources of PAHs [58].

Profiles of PAHs from the iron and steel industries have shown that PAH emission compositions are inherently variable with respect to combustion sources [59,60]. The combustion of heavy oil produced considerably higher concentrations of 4, 5 and 6 or 7-ring PAHs than the other sources and these particular PAHs may be more harmful to humans [56]. Fig. 2 shows that component 2 was

Table 2
Eigenvectors obtained by principal component analysis of the PAHs measured in passive air samplers in both seasons.

Variable	Component 1	Component 2	Component 3
FLU	**0.78**	−0.63	−0.09
PHE	0.62	−0.52	−0.58
ANT	0.50	0.31	**0.81**
PYR	**0.99**	−0.11	0.03
BaA	−0.54	**−0.75**	0.38
CHR	**0.99**	0.04	0.11
BbF	**0.78**	0.54	−0.32
BkF	**0.93**	0.37	0.06
BaP	**0.89**	0.06	0.44
DBA	−0.26	**0.92**	−0.28
BPE	**0.94**	−0.27	−0.19
Eigenvalues	6.73	2.69	1.58
Accumulated variance (%)	61.16	85.66	99.01

In bold, loading values ≥0.70.
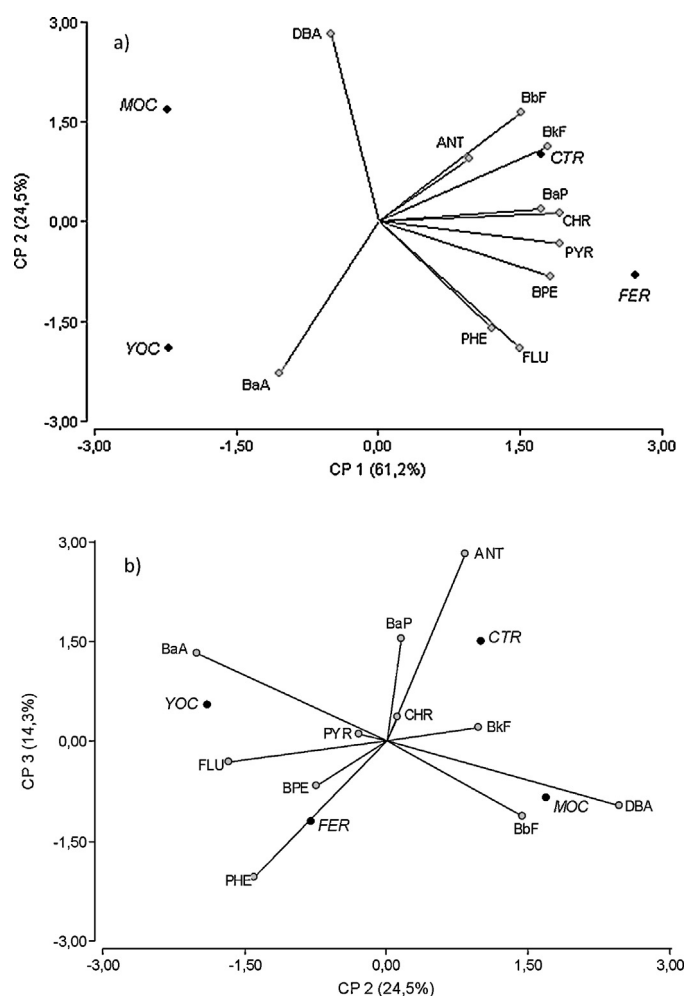
Fig. 2. Biplots based on the first and second components (a) and the second and third components (b) of the principal components analysis for PAH concentrations in PAS, using different sites as the classification criteria.

related to the YOC site (BaA source) and the MOC site (source DBA). This can be explained as the main emission source at YOC site is a cement plant that uses natural gas as its primary fuel (75%), which therefore might be the source of the high concentrations of BaA in this site (Table 1). Related to this, it is known from several other studies that the combustion of natural gas is considered to be a source of BaA [60–62].

With respect to the MOC site, the DBA values were higher in the dry season, which might be explained by the proximity of the site to the National Route 19 or also by fuel storage plant emissions. Bixiong et al. [63] also mentioned that DBA predominated in gasoline engine exhausts. The third component was marked by variable ANT, which has been shown to be a tracer of coal combustion in previous studies [64,65]. Fig. 2 shows that this component was associated with the CTR site, indicating the contribution of domestic emissions at this site. These emissions are predominantly associated with the burning of coal, oil, gas, garbage, or other organic substances such as tobacco or char broiled meat [55]. In urban areas where coal, wood, and peat burning are predominant, a high proportion of the PAH ambient air concentration is associated with these sources [59].

PAHs in T. capillaris

Table 3 shows the concentrations of each of the PAHs (LMW, HMW and total) measured in leaves of *T. capillaris* at the basal site

and at each study site after 90 days of exposure. The total concentrations of PAHs found in *T. capillaris* were in the range from 231 ng g^{-1} (Site MOC) to 532 ng g^{-1} (site FER). When compared with previous studies, our results were lower than those found in *T. capillaris* in the city of Stuttgart, Germany with exposure for 12 weeks [33]. On the other hand, a recent study of Murakami et al. [66] compared the abilities of five deciduous tree species for recording PAH accumulation, and concluded that *Ginkgo biloba* L. presented the highest accumulation of total PAHs (circa 180 ng g^{-1} DW), thus recommending this species as a biomonitor for these compounds. However, in this study the total concentrations of PAHs found in *T. capillaris* were greater than those found for *Ginkgo biloba* L.

With regard to the different seasonal concentrations of Σ LMW, the PAHs at all sites of exposure (except MOC) were higher in the dry season, and the Σ HMW PAHs concentrations were also higher (except YOC) at this time. In addition, the EB ratio values observed in the dry season for all the HMW PAHs analyzed had values greater than 1.75, which are considered by Frati et al. [47] as representing severe accumulation. The wet season showed severe accumulation for the PAHs: PHE, PYR, BaA, CHR, BbF, DBA and BPE, indicating a lower accumulation of the biomonitor in this season, coinciding with the results found in the passive air samplers. With respect to differences between different sites, it was observed that the sites which had a greater number of PAHs with severe accumulations (EB ratio > 1.75) were CTR (PYR, BaA, BbF, BkF, BaP, DBA, BPE) and FER (PHE, PYR, BaA, CHR, BbF, BkF, DBA and BPE) for the dry season, whereas in the wet season the FER site had the highest number of PAHs with severe accumulation (PHE, PYR, BaA, CHR, BbF, DBA and BPE).

Finally, the PAH values obtained in *T. capillaris* leaves for the dry season showed a similar pattern to those obtained in the PAS, with concentrations of PYR, BbF, BkF, DBA being highest at sites located in the city of Córdoba (FER and CTR), the concentration of ANT being highest at the CTR site, the concentration of BaA being highest at the YOC site and the concentration of DBA being highest at the MOC site, thus repeating the same pattern as that found in the PAS. The PAH profiles in *T. capillaris* and PAS for the two seasons can be seen in the supplemental material (Figs. S2–S5).

Correlation between PAHs concentrations in passive air samplers and T. capillaris

Table 4 shows the correlations between the PAH accumulation in leaves of *T. capillaris* and the concentrations found in the passive
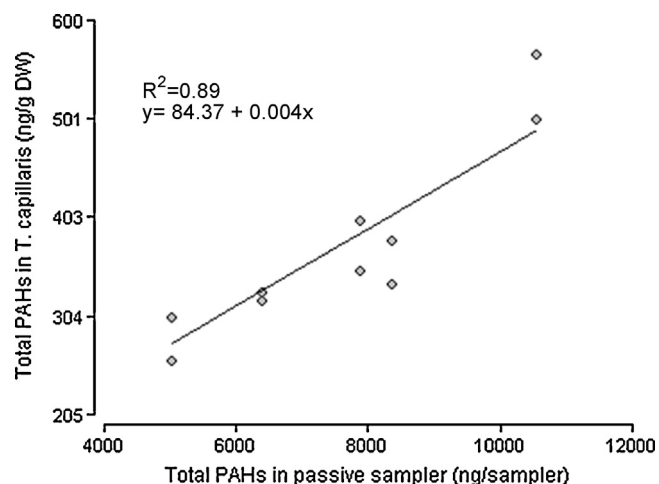
Fig. 3. Relationship between the concentration of PAHs measured in the PAS and in the biomonitor.

Table 3
Concentrations of PAHs and the exposed to basal ratio (EB ratio) in *Tillandsia capillaris* from the different sites.

PAHs (ng/gDW)	Basal Mean (n = 3)	CTR Mean (n = 3) (EB ratio)	FER Mean (n = 3) (EB ratio)	YOC Mean (n = 3) (EB ratio)	MOC Mean (n = 3) (EB ratio)
Dry season, 21st March–21st June (rain 81.6 mm)					
FLU	25.23	36.42 (1.44)	30.18 (1.20)	30.63 (1.21)	40.78 (1.61)
PHE	114.80	165.55 (1.44)	365.24 (3.18)	254.92 (2.22)	121.55 (1.06)
ANT	2.15	3.47 (1.61)	2.37 (1.10)	3.06 (1.42)	2.81 (1.31)
PYR	17.91	68.43 (3.82)	85.74 (4.79)	21.03 (1.17)	37.04 (2.07)
BaA	1.30	4.84 (3.72)	4.72 (3.62)	6.28 (4.83)	4.41 (3.39)
CHR	4.48	6.98 (1.56)	8.47 (1.89)	8.68 (1.94)	5.92 (1.32)
BbF	8.28	19.94 (2.40)	20.84 (2.52)	15.06 (1.81)	10.29 (1.24)
BkF	0.22	0.40 (1.81)	0.39 (1.77)	0.29 (1.32)	0.33 (1.49)
BaP	0.27	0.56(2.07)	0.37 (1.37)	0.41 (1.52)	0.40 (1.49)
DBA	3.37	9.88(2.93)	7.17 (2.13)	10.20 (3.03)	11.03 (3.27)
BPE	1.93	6.38(3.31)	6.98 (3.62)	5.67 (2.94)	1.81 (0.94)
Σ LMW	142.17	205.44(1.45)	397.79 (2.79)	288.61 (2.03)	165.14 (1.16)
Σ HMW	37.76	117.41(3.11)	134.33 (3.56)	67.64 (1.79)	71.23 (1.89)
Total PAHs	179.93	322.86 (1.79)	532.12 (2.96)	356.25 (1.97)	236.37 (1.31)
Rainy season, 1st September–1st December (rain 157.5 mm)					
FLU	28.38	33.78 (1.19)	29.21 (1.03)	38.71 (1.36)	29.53 (1.04)
PHE	108.53	123.83 (1.14)	217.55 (2.00)	120.45 (1.11)	208.16 (1.92)
ANT	1.93	1.90 (0.98)	3.38 (1.75)	1.71 (0.89)	1.90 (0.98)
PYR	25.87	48.70 (1.88)	70.68 (2.73)	44.16 (1.71)	11.98 (0.46)
BaA	1.43	0.47 (0.33)	3.73 (2.61)	3.05 (2.14)	1.45 (1.01)
CHR	3.52	3.83 (1.09)	8.42 (2.39)	5.20 (1.48)	6.07 (1.72)
BbF	9.22	12.98 (1.41)	20.87 (2.26)	14.83 (1.61)	10.14 (1.10)
BkF	0.27	0.25 (0.91)	0.45 (1.68)	0.25 (0.92)	0.22 (0.82)
BaP	0.30	0.22 (0.72)	0.34 (1.13)	0.40 (1.33)	0.26 (0.85)
DBA	5.36	7.19 (1.34)	10.92 (2.04)	9.44 (1.76)	10.09 (1.88)
BPE	1.06	8.00 (7.51)	8.39 (7.88)	5.40 (5.07)	0.78 (0.73)
Σ LMW	138.84	159.52 (1.15)	250.18 (1.80)	160.87 (1.15)	239.59 (1.73)
Σ HMW	47.03	81.63 (1.74)	123.80 (2.65)	82.74 (1.76)	40.99 (0.87)
Total PAHs	185.86	241.15 (1.30)	373.99 (2.02)	243.61 (1.31)	280.58 (1.51)

Σ LMW: sum of three-ring PAHs; Σ HMW: sum of four and five-ring PAHs.

air samplers, with a larger number of significant correlations occurring in the dry season. This could have been due to the lower concentrations found in the air during the wet season, or on the other hand, due to rain washout of PAH in the biomonitor. In addition, the correlation coefficients obtained for the LMW were higher in the two sampling periods than the correlation coefficients obtained for the HMW. Previous studies using biomonitors [66,67] found significant correlation coefficients between concentrations of HMW PAHs in biomonitors with concentrations found in the air in the particulate phase. When considering the sum of all PAHs for both sampling periods, a strong positive correlation ($R^2 = 0.89$) can be seen between the

concentrations found in the leaves of *T. capillaris* (Fig. 3) and those obtained in the PAS. We tested different systems of equations and found that at low concentrations found in the PAS (less than 3000 ng sampler^{-1}) the biomonitor does not have a good response and therefore does not allow determining the differences between the sites. However, if we only use the data of the sites where the concentration of PAHs in PAS was greater than 3000 ng sampler^{-1}, we can observe a good fit of the data to a lineal regression (Fig. 2). This could be the reason why the biomonitor showed a better response in the dry season, as total PAH values at this season were higher than those found in the rainy season.

Nevertheless, in our study *T. capillaris* reflected the PAH concentrations in the air for the dry station, and under these conditions it can be used as a biomonitoring tool.

Conclusions

The concentrations of PAHs from the air of different sites in the province of Córdoba showed dependency on environmental conditions (seasonal differences) as well as on the presence of emission sources at each study site. The PAS was a useful tool to observe differences in the concentrations of PAHs between the study periods, with these being higher in autumn (dry season), which may be attributed to the different environmental conditions occurring during this period (lower temperatures and precipitation levels). With respect to the different sites, higher concentrations of PAHs were observed at the industrial site, and a large amount of PAHs were associated with the urban and industrial sources present in the city of Córdoba (FLU, BPE, PYR, CHR, BaP, BkF and BbF). The concentration of ANT was associated with the presence of domestic sources (CTR), and the cement plant at the site YOC was shown to be an important source of BaA, which could be related to the use of natural gas as fuel. At the MOC site, DBA enrichment was

Table 4
Pearson's correlation coefficient between each PAH measured in the passive air sampler and in the biomonitor.

PAHs (ng/gDW)	Dry season	Rainy season
FLU	−0.57	−0.49
PHE	0.91[**]	0.83[*]
ANT	0.64	−0.20
PYR	0.92[**]	0.09
BaA	0.83[*]	0.25
CHR	0.41	0.39
BbF	0.82[*]	0.03
BkF	0.47	0.32
BaP	0.38	−0.64
DBA	0.51	−0.38
BPE	0.68[*]	0.71[*]
Σ LMW	0.93[***]	0.80[*]
Σ HMW	0.91[***]	0.14
Total PAHs	0.94[***]	0.85[**]

[*] Significant with $P \leq 0.05$
[**] Significant with $P \leq 0.01$
[***] Significant with $P \leq 0.001$.

observed, which we associated with vehicle source in this area. *T. capillaris* was demonstrated to be a good accumulator of PAHs, considering that it reflected seasonal differences between different sites and that these were similar to those found in the passive samplers for the dry season. The correlations between the concentrations found in the biomonitor and air were better for the Σ LMW PAHs with respect to Σ HMW. In conclusion, *T. capillaris*, as mentioned in previous studies, can be used as a suitable biomonitor of concentrations of PAHs in the environment and further studies must be performed with regard to rainfall washout rates to optimize its use in biomonitoring programs.

Conflict of interest

None declared.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jece.2013.08.012.

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