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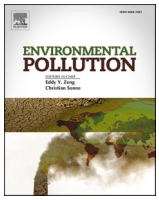

Tracking polycyclic aromatic hydrocarbons (PAHs) across Palermo with the invasive grass *Cenchrus setaceus* (syn. *Pennisetum setaceum*)

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants posing significant environmental and health risks. This study evaluates the suitability of the invasive grass *Cenchrus setaceus* (syn. *Pennisetum setaceum*) as a passive collector of PAHs contamination across urban and coastal areas of Palermo, Sicily. Sampling campaigns were conducted in August and December at 12 sites characterised by varying levels of traffic intensity and anthropogenic pressure. Sixteen priority PAHs were extracted from inflorescence tissues and quantified by GC-MS in selected ion monitoring mode. Seasonal variations in PAH concentrations, with total levels ranging from 86.2 to 254.1 ng g^{-1} in summer and from 49.4 to 1217 ng g^{-1} in winter, were confirmed by a one-way PERMANOVA ($p = 0.0042$). Low molecular weight PAHs predominated in summer, whereas intermediate and high molecular weight PAHs increased in winter. This reflects temperature-dependent gas-particle partitioning, deposition processes and emission patterns. Diagnostic isomeric ratios indicated predominantly mixed sources of PAHs, mainly driven by vehicular traffic and liquid fossil fuel combustion, with additional contributions from biomass and coal combustion, as well as minor petrogenic contributions. Our results demonstrate that *C. setaceus*, which is widely distributed along road verges and anthropized habitats, effectively integrates atmospheric PAHs deposition over time. This supports its potential use as a passive biomonitor. Furthermore, incorporating this species into urban and coastal environmental assessments could facilitate dual management, enabling contamination monitoring while promoting the valorisation of biomass into high value-added bio-based products within circular economy strategies.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of two or more fused aromatic rings primarily generated through the incomplete combustion of organic materials including fossil fuels and biomass (Orecchio et al., 2016a; Kotnala et al., 2026; Joshi et al., 2026).

PAHs are highly lipophilic semi-volatile compounds that persist in the environment and readily partition between the gas phase and atmospheric particulate matter (PM) (Das et al., 2025).

Lower molecular weight PAHs (LMW-PAHs: 2–3 rings) are typically found in the vapour phase, whereas higher molecular weight PAHs (HMW-PAHs: 5–6 rings) are mainly associated with fine particles such as $PM_{2.5}$, which increases their atmospheric residence time and potential health impact. Moderately volatile compounds with an intermediate molecular weight (IMW-PAHs: 4-rings) exhibit temperature-dependent gas–particle partitioning and can be found in both phases (Ferreira Azevedo et al., 2025).

From a toxicological perspective, PAHs are of major concern because several members of this class are carcinogenic and mutagenic. The International Agency for Research on Cancer has designated 16 PAHs as priority compounds, including benzo[a]pyrene (BaP), which is classified as a Group 1 human carcinogen and is widely used as a marker of the carcinogenic potency of PAH mixtures. Under Regulation (EC) No 1272/

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2008 (CLP Regulation), BaP is consistently classified in the European Union as a Category 1B carcinogen (Balducci et al., 2026).

PAHs are ubiquitous environmental contaminants that are detected in the air, water, soil, sediments, vegetation, and food. Following their emission into the atmosphere, they undergo dry and wet deposition, which results in the contamination of terrestrial and aquatic ecosystems, and their subsequent transfer through food webs (Yacoubi et al., 2023; Cai et al., 2026). Soil is a significant environmental reservoir for PAHs, receiving inputs from atmospheric deposition, wastewater discharge and irrigation practices (Feng et al., 2025; Kaur et al., 2026). However, it is primarily above-ground plant tissues that reflect atmospheric contamination, since the uptake of PAHs from soil by roots is generally limited by their strong hydrophobicity and low bioavailability (Zeng et al., 2025).

Plants play a key role in intercepting airborne PAHs, acting as passive samplers of atmospheric contamination (Huang et al., 2018). Deposition onto aerial parts depends on air concentrations, gas–particle partitioning behavior, and environmental conditions, as well as species-specific morphological and biochemical characteristics (Ossola and Farmer, 2024). The efficiency of particle capture and retention are influenced by plant surface area, cuticular wax, and lipid content, with smaller, hairy, lipid-rich leaves retaining higher amounts of particle-bound PAHs (De Nicola et al., 2016). In addition, seasonal variability and meteorological factors further modulate accumulation patterns (Zhang et al., 2025).

Biomonitoring using wild and cultivated plants and/or their tissues offers a cost-effective, complementary strategy for assessing atmospheric PAHs contamination over wide areas and extended timeframes (Sulistiyorini et al., 2022; Dhara and Dutta, 2025). Unlike active sampling, vegetation integrates pollutant deposition over time, providing information that is representative of the area in terms of both emission sources and contamination gradients.

Among the various organisms used for biomonitoring, invasive species offer unique opportunities due to their characteristics. Their adaptability, resilience, and wide distribution enable the assessment of contaminant bioaccumulation, particularly in degraded habitats where native species are scarce or protected, thereby minimising additional ecological stress (Pastorino et al., 2025).

Cenchrus setaceus (Forssk) Morrone (syn. Pennisetum setaceum (Forssk) Chiov.) is a perennial grass that is native to North and East Africa, the Near East, and the Arabian Peninsula, primarily occurring in seasonally dry tropical biomes (Sohrabi et al., 2026). Due to its ornamental value, it has been widely introduced beyond its native range and is now considered thermocosmopolitan.

Its adaptability, drought tolerance, prolific seed production, and fire-promoting traits, together with its ecological history, enhance its competitive advantage and invasiveness, allowing rapid spread from urban areas into arid and semi-arid coastal habitats (Sohrabi et al., 2026; Pasta et al., 2010).

C. setaceus is recognized as a problematic invasive species worldwide, having invaded temperate regions of South Africa, Indonesia, North America, the Caribbean, Oceania, and more recently the Mediterranean basin (Pasta et al., 2010; Sohrabi et al., 2026). It has been identified as high priority in Europe through pest risk analysis and is listed as an invasive alien species of union concern under EU 1143/2014 Regulation (Sohrabi et al., 2026).

Within the Mediterranean region, *C. setaceus* has expanded particularly rapidly in coastal and semi-arid environments, where it exhibits strong competitive ability and high ecological plasticity. In Sicily, the spread of this species has been documented not only along the coast, but also in inland habitats and on smaller islands such as Pantelleria Island (Minissale et al., 2023). From an ecological perspective, the invasion of *C. setaceus* is especially worrying because it actively replaces native species, thereby altering the structure and functioning of local plant communities. As reported by Guarino et al. (2021), *C. setaceus* can outcompete the native *Hyparrhenia hirta* for dominance in perennial grasslands on stony coastal sites. This shift in dominance may lead to reduced biodiversity, changes in fire regimes, and long-term ecosystem transformation.

Due to its extensive distribution in highly anthropized and marginal habitats, *Cenchrus setaceus* may represent an opportunity beyond its invasive character (Rahlao et al., 2010). In Sicily, especially within the urban and peri-urban areas of Palermo, this species commonly colonizes road verges and other disturbed sites exposed to vehicular emissions. Its tolerance to poor soil, drought, and pollution makes *C. setaceus* a stable component of traffic-affected areas, and its widespread presence along roadsides suggests it could serve as an effective passive collector of atmospheric PAHs in urban settings. In addition, previous studies have demonstrated the promising potential of *Pennisetum* spp. and their associated rhizosphere for phytoremediation applications of heavy metals (Hong et al., 2025) as well as organic pollutants (Onifade et al., 2023), including PAHs (Bello et al., 2022; Riskuwa-Shehu et al., 2022; Harry et al., 2025). Furthermore, the significant biomass production of this species has been investigated in relation to biomass valorisation, which supports its potential role in integrated remediation and resource-recovery strategies. For instance, *P. setaceum* fibres have been used to improve the thermomechanical and insulation properties of bio-based construction materials, while *Pennisetum purpureum* shows potential for bioenergy valorisation (Osman et al., 2020; Charai et al., 2022).

Several studies on *Pennisetum* species have focused on their ecology, phytoremediation, and biomass potential (Zhang et al., 2024).

To the best of our knowledge, this is the first study to evaluate the suitability of *C. setaceus* as a biomonitor of PAHs. The case study focused on areas of Palermo (Sicily) with varying anthropogenic pressure, including urban sites with heavy traffic and coastal sites with a seaside vocation, which are much less frequented in winter. To account for potential seasonal variability in traffic intensity, atmospheric deposition, and human activity, sampling campaigns were conducted during both the summer and winter seasons. This spatial and temporal gradient enables us to evaluate whether PAHs accumulation patterns and compositional profiles in *C. setaceus* reflect differences in site typology and seasonal anthropogenic pressure.

This study aims to contribute to a shift in perspective by exploring the potential to transform a widespread invasive species from a management concern into a functional ecological resource. It seeks to support the development of more sustainable and management-oriented strategies for assessing the environmental quality of urban and coastal areas by integrating biomonitoring, seasonal assessment, and biomass valorisation within eradication frameworks.

2. Materials and methods

2.1. Site and sampling campaign

Palermo is Sicily's largest city and one of Italy's most populous, with 625,000 inhabitants spread across its municipal area. Central and semi-central districts are high density due to administrative, commercial and service activities, and long-established urban structure. In contrast, the coast is less densely populated with dispersed settlements and more open spaces. There is marked seasonal variation in population density, with a significant increase in summer due to tourism, followed by a decrease in winter. These dynamics result in a heterogeneous territory with variations in anthropogenic pressure.

Samples of *C. setaceus* were collected from 12 different sites across the Palermo area in August and then re-sampled at the same sites in December. The same plant tissue (inflorescence) was consistently collected in both sampling campaigns. These sites are described in Table S1 and shown in Fig. 1.

The sampling sites were selected based on their varying exposure to anthropogenic pressures, particularly vehicular traffic. All samples were collected in areas adjacent to the road pavement (see Fig. S1).

Label	Sampling Site	Coordinates
1	Via Mongerbino	38°08'30"N 13°19'38"E
2	Viale Regione Siciliana	38°08'08"N 13°19'51"E
3	Corso Calatafimi	38°06'09"N 13°19'50"E
4	Via del Vespro	38°06'12"N 13°21'44"E
5	Via Buonriposo	38°06'06"N 13°22'24"E
6	Via Salvatore Cappello	38°06'12"N 13°22'44"E
7	Via Messina Marine	38°06'21"N 13°23'13"E
8	Via Antonino Laudicina	38°05'35"N 13°24'38"E
9	Piazza Figurella	38°04'54"N 13°26'06"E
10	Santa Flavia	38°05'42"N 13°32'09"E
11	Casteldaccia	38°03'22"N 13°32'05"E
12	Lascari	37°59'57"N 13°53'46"E

Fig. 1. Locations of *C. setaceus* sampling sites in Palermo, Sicily. Map image courtesy of Google Earth Pro.

Re-sampling in a different season aimed to evaluate seasonal variations in contamination, focusing particularly on sites characterised by lower anthropogenic pressure, such as the coastal areas of Santa Flavia and Lascari, which have a predominantly seaside vocation and greater vegetation cover. It was hypothesized that the seasonal variation in traffic intensity between summer and winter could influence PAH contamination level in these sites. The sampling strategy was therefore designed to evaluate the suitability of *C. setaceus* as a potential passive sampler of PAH contamination when considering seasonal variations in anthropogenic pressures, particularly those related to vehicular traffic. Samples were collected using scissors and placed in paper bags inside a refrigerated box. They were then transported to the laboratory and stored at - 20 °C until extraction.

2.2. Chemicals and reagents

Sodium sulfate anhydrous (≥99 %) was purchased from Sigma-Aldrich. Florisil (60–100 mesh) was obtained from Merck. Dichloromethane (HPLC grade) and *n*-hexane (GC–MS grade) were purchased from Carlo Erba Reagents.

A native standard solution containing 16 PAHs: naphthalene (N), acenaphthylene (Apl), acenaphthene (Apt), fluorene (F), phenanthrene (P), anthracene (A), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (BA), chrysene (Cy), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaPy), indeno[1,2,3-cd]pyrene (I), dibenz[a,h] anthracene (D), and benzo[ghi]perylene (B) was purchased from Ultra Scientific Italia Srl (PAH Mixture, 2000 mg L^{-1} in methylene chloride/benzene 1:1, US-106N-1).

The deuterated internal standards included deuterated PAHs Mix A (ISM-740A-1), containing three analytes (acenaphthylene-d_8, chrysene-d_{12}, indeno[1,2,3-cd]pyrene-d_{12}) at 200 mg L^{-1} in toluene, and deuterated PAHs Mix B (ISM-750-1), containing seven analytes (acenaphthene-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, benzo[a]anthracene-d_{12}, benzo[a]pyrene-d_{12}, dibenz[a,h]anthracene-d_{14}, dibenz[a,i] pyrene-d_{14}) at 200 mg L^{-1} in methylene chloride. Both mixes were purchased from Ultra Scientific Italia Srl.

The complete list of native and deuterated standards is reported in Table S2.

2.3. Extraction of PAHs from C. setaceus samples

The extraction procedures were developed and optimized based on protocols previously reported, with minor modifications (De Nicola et al., 2016; Yang et al., 2022; Okwute et al., 2025). Samples were not washed prior to extraction in order to preserve both surface-deposited and tissue-associated PAHs.

In brief, the inflorescence portion of the plant material was cut into small fragments, homogenized, weighed, and transferred into a flask for PAH extraction. For each 2 g sample, 25 μL of a surrogate standard solution (20 mg L^{-1}, deuterated PAH Mix A) was added, followed by anhydrous sodium sulfate (sample: salt ratio 1:2, w/w). Extraction was performed using a 50 mL of a n-hexane/dichloromethane mixture (1:1, v/v) in an ultrasonic bath for 45 min at 25 °C.

The sonicated extract was transferred to a new flask along with 10 × 2 mL portions of the extraction solvent used to rinse the original flask, in order to recover any residual analytes. This was subsequently concentrated to ~2 mL using a rotary evaporator. Purification was then carried out using Pasteur pipette columns that had been packed with glass wool, Florisil, and anhydrous sodium sulfate. These columns had been preconditioned with the extraction solvent according to EPA Method 3620C. After sample loading, the column was eluted with 3 × 5 mL of the same solvent mixture. The purified extract was finally concentrated to 500 μL and transferred to a vial together with 500 μL of an internal standard solution (0.2 mg L^{-1}, Deuterated PAH Mix B). The concentrations presented in this research are therefore expressed in wet weight (w.w.). Deuterated standards were added to both the samples and the calibration standards.

For calibration purposes, serial dilutions of the native standards were prepared to achieve final concentrations of 0.1, 0.5, 1, 5, 10, 25, 50, 100, 200, and 400 μg L^{-1}.

Quantification was performed using the internal standard method, which is based on the ratio of the peak area of each native analyte to that of its corresponding deuterated internal standard. This standard is added to both the calibration standards and the sample extracts. This compensates for variations in the instrumental response by normalizing the signal. The coefficients of determination (R^2) of the calibration curves were close to the theoretical value of 1, demonstrating excellent linearity over the investigated concentration range (Fig. S2).

Mix A, which contains three deuterated PAHs, was added prior to the extraction step as a recovery standard to assess the efficiency of the extraction process. Recovery was calculated for each sample by substituting the signal obtained from the deuterated analyte into the calibration curve equation as the unknown variable. The resulting concentration was then converted into a percentage recovery and the

corresponding correction factor applied to each sample.

Concurrently with the qualitative and quantitative analysis of PAHs, the instrumental limits of detection (iLOD) and quantification (iLOQ) were determined by analysing 10 blanks. For each PAH, the iLOD was determined as the mean blank response plus three times the standard deviation, and the iLOQ as the mean blank response plus ten times the standard deviation (Wenzl et al., 2016).

The iLOD and iLOQ, expressed in ng mL^{-1}, were converted into sample-related values (ng g^{-1}) to obtain the LOD and LOQ of samples (sLOD and sLOQ respectively) considering the extraction procedure (2 g of sample brought to a final volume of 1 mL). This was calculated according to the following equation:

$$sLOD = (iLOD \times \text{final volume}) / \text{sample weight}$$

$$sLOD\ (ng\ g^{-1}) = (iLOD\ (ng\ mL^{-1}) \times 1\ mL)\ /\ 2g$$

$$sLOD = iLOD \times 0.5\ (ng\ g^{-1})$$

All sLOD and sLOQ values are reported in Table S3.

All samples were analysed in triplicate using GC-MS. The relative standard deviation (RSD) of replicate measurements for individual compounds ranged from 10 % to 20 %.

2.4. GC-MS analysis of PAHs

GC-MS analysis of PAHs was performed in selected ion monitoring (SIM) mode using a Shimadzu QP-2010 Plus system equipped with an AOC-20i autosampler (Shimadzu, Kyoto, Japan) and a gas chromatograph fitted with a non-polar capillary column (DB-5-MS Ultra Inert; Agilent J&W) of 30 m × 0.25 mm (i.d.) with a 0.25 μm film thickness, coupled to a data acquisition system.

The oven temperature program was as follows: initial hold at 50 °C for 2 min, ramped at 18 °C/min to 240 °C and held for 6 min, followed by a ramp of 20 °C/min to 320 °C and held for 10.44 min. The ion source temperature was set at 260 °C, the GC-MS interface (transfer line) at 300 °C and the injector at 280 °C. Helium was used as the carrier gas at a flow rate of 1 mL/min. The injection volume was 1 μL in splitless mode, with a total run time of 33 min. A solvent delay of 5.1 min was applied to prevent solvent signals from entering the detector.

After determining the retention times of the individual analytes, three SIM time windows were established (5.5–12.0 min, 12.0–23.5 min, 23.5–32.9 min) to focus detection on the target PAHs. Within each window, quantification and confirmation ions of the eluting PAHs were monitored. Mass spectra were acquired in electron impact (EI) mode at 70 eV. The column operated under constant pressure conditions (53.6 kPa), with helium as the carrier gas and a linear velocity of 36.3 cm/s.

To prevent cross-contamination between consecutive analyses, a standardised syringe washing protocol using a n-hexane/dichloromethane solution (1:1, v/v) was implemented, comprising four wash cycles before sample injection, four cycles after injection, and two conditioning cycles with the sample. Given the widespread presence of PAHs, procedural blanks were injected between analytical duplicates and between subsequent samples to monitor and minimise potential background contamination.

Table S2 shows the retention times and the percentage recovery obtained for all the considered PAHs, as well as the individual fragments acquired in SIM mode. Furthermore, Fig. S3 presents the chromatogram of a standard solution containing both native and deuterated PAHs.

2.5. Isomeric indices

PAH sources in the analysed matrices and environments were assessed using diagnostic approaches reported in previous studies (Mannino and Orecchio, 2008; Bergamasco et al., 2014; Orecchio et al., 2016b; Orecchio et al., 2022) (see Table 1).

Table 1
Diagnostic isomeric ratios of selected PAHs for potential emission sources.

Isomeric ratio	Range of values	Possible source interpretation
A/(A + P)	<0.10	Low-temperature (petrogenic) sources
	>0.10	Predominance of combustion processes
Fl/(Fl + Py)	<0.40	Petrogenic sources
	0.40 - 0.50	Combustion of liquid fossil fuels (vehicular traffic, crude oil)
	>0.50	Biomass, coal, or wood combustion
BA/(BA + Cy)	<0.20	Petrogenic sources
	0.20 - 0.35	Mixed sources (petrogenic/combustion)
	>0.35	Predominance of combustion processes
I/(I + B)	<0.20	Petrogenic sources
	0.20 - 0.50	Combustion of liquid fossil fuels (vehicular traffic)
	>0.50	Biomass and coal combustion

Potential PAH sources were inferred by calculating selected diagnostic ratios, including A/(A + P), Fl/(Fl + Py), BA/(BA + Cy), and I/(I + B).

These molecular indices are commonly used to distinguish between petrogenic (petroleum-derived) and pyrogenic (combustion-related) sources. In particular, these ratios allow differentiation between unburned fossil fuel sources and high-temperature combustion processes. Moreover, some of these ratios provide additional resolution among combustion sources, enabling distinction between, for example, petroleum combustion and biomass or coal burning, as summarized in Table 1.

2.6. Statistical analysis

Seasonal differences in the multivariate profiles of 16 PAHs across 12 sites were tested using a one-way PERMANOVA. Prior to analysis, values below the limit of quantification were replaced with LOQ/2, and all data were log-transformed to reduce skewness and the influence of extreme values. The analysis was conducted using Euclidean distances with 9999 permutations to assess statistical significance, performed in PAST version 4.04 (Hammer and Harper, 2024).

3. Results and discussion

Considering the territorial heterogeneity and seasonal variability, PAHs were analysed in *C. setaceus* samples collected from different sectors of Palermo during summer and winter. This approach aimed to assess potential differences in PAH contamination levels between different areas and seasons. Tables S4 and S5 show the concentrations of 16 PAHs and their sum (Σ) found in *C. setaceus* samples collected in August and December, respectively. The total concentration of the 16 PAHs in summer ranged from 86.2 to 254 ng g^{-1}, whereas in winter it ranged from 49.1 to 1217 ng g^{-1}. While summer concentrations of ΣPAHs were relatively consistent across different sampling sites, the lowest levels were recorded at Via Salvatore Cappello and Casteldaccia (86.2 and 88.4 ng g^{-1}, respectively), and the highest concentration (254 ng g^{-1}) was observed at Via del Vespro, where all investigated PAHs were detected. In winter, a higher variability among sites was observed. The lowest concentrations were recorded at sites considered less polluted, based on their lower anthropogenic pressure and reduced vehicular traffic (Table S1); ΣPAHs in *C. setaceus* samples from Santa Flavia and Lascari were 49.4 and 49.1 ng g^{-1}, respectively, whereas the highest concentration (1217 ng g^{-1}) was measured at Corso Calatafimi, characterised by both slow and intense traffic.

The one-way PERMANOVA indicated a significant effect of season on the multivariate profiles of the 16 PAHs (pseudo-F = 5.199, p = 0.0042). This finding indicates that there were considerable variations in the chemical composition between seasons.

Seasonal differences in PAHs concentrations may result from multiple physicochemical, biological and environmental factors, including the effects of temperature on volatility, atmospheric transport and

dispersion, photodegradation, humidity, atmospheric pressure, the growth stage of plants, the composition of the rhizosphere, and microbial activity (Zhao et al., 2018; Zhou et al., 2020). Lower summer PAHs concentrations likely reflect enhanced volatilization and degradation, whereas winter conditions, with lower temperatures and thermal inversions, favour accumulation. A comparison of summer and winter data indicates that heavier PAHs increase in winter, likely due to greater production during this period, lower volatility, and higher environmental persistence.

Benzo(a)anthracene was detected at low concentrations in summer at 9 out of 12 sites (0.95 - 2.16 % of total PAHs). In winter, however, it was found at higher concentrations and with a greater relative contribution in 11 out of 12 sites (1.96 - 5.77 % of total PAHs). During the summer, low-molecular-weight PAHs (2 - 3 rings) dominated at all sites, accounting for a mean of 59.64 % (range 35.25 - 72.21 %), while intermediate-weight PAHs (4 rings) accounted for 7.79 - 31.41 % (mean 20.07 %). High-molecular-weight PAHs (5 - 6 rings) varied from 5.63 % at Via Antonino Laudicina to 46.26 % at Lascari, averaging 20.29 % (Fig. 2a).

Conversely, in winter, the lighter PAHs accounted for 12.85 - 66.92 % (mean: 33.86 %) of the total PAHs at each site, the intermediate-weight PAHs for 15.15 - 62.20 % (mean: 39.73 %), and the heavier PAHs for 12.15 - 55.86 % (mean: 26.41 %) (Fig. 2b).

These results highlight pronounced seasonal variability in PAH distribution according to ring number. During summer, LMW PAHs predominate due to their high volatility and prevalence in the atmospheric

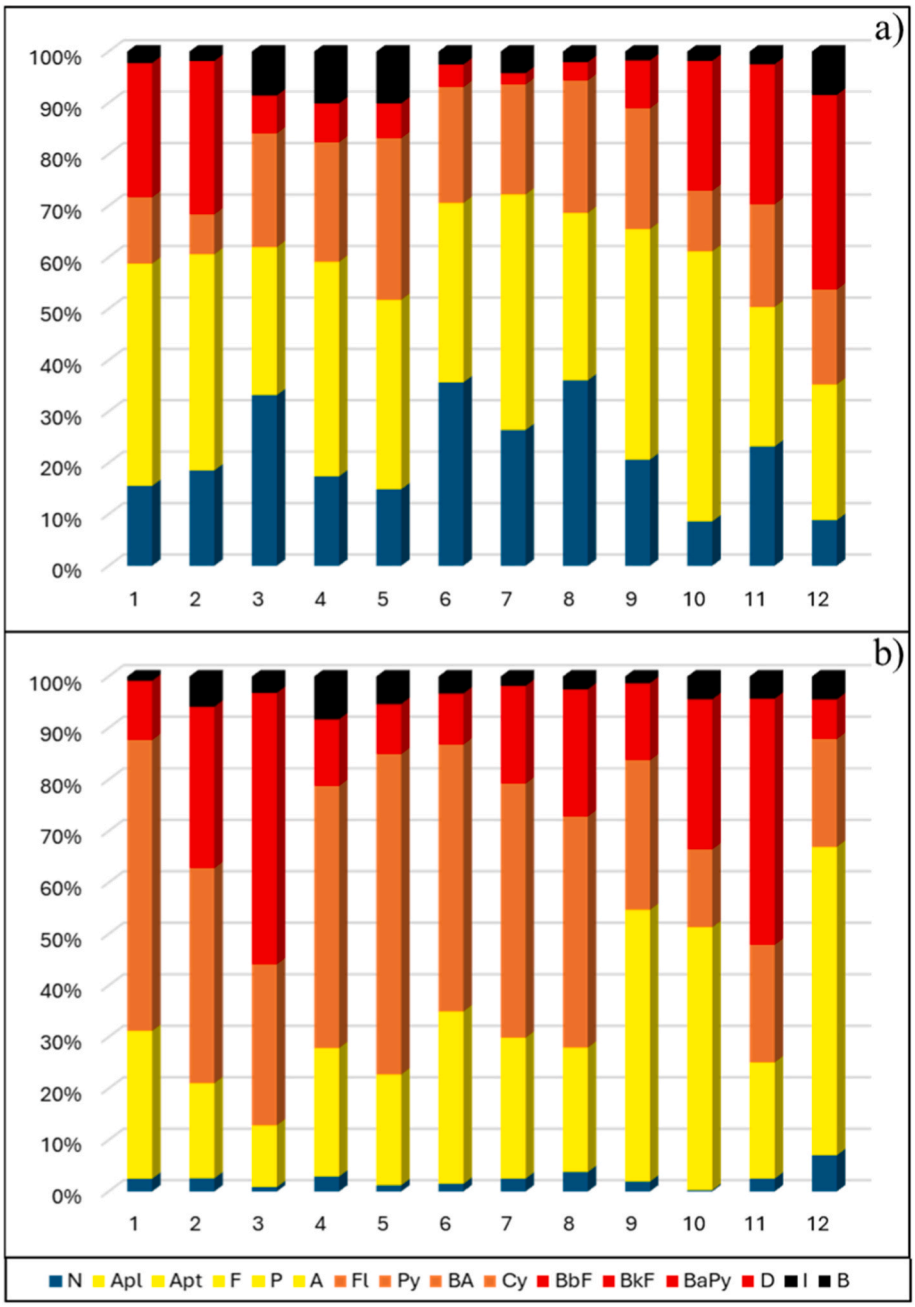

Fig. 2. Percentages of PAHs with 2 rings (blue), 3 rings (yellow), 4 rings (orange), 5 rings (red), and 6 rings (black) at each site in August (a) and in December (b). 1 = Via Mongerbino; 2 = Viale Regione Siciliana; 3 = Corso Calatafimi; 4 = Via del Vespro; 5 = Via Buonriposo; 6 = Via Salvatore Cappello; 7 = Via Messina Marine; 8 = Via Antonino Laudicina; 9 = Piazza Figurella; 10 = Santa Flavia; 11 = Casteldaccia; 12 = Lascari. Values < LOQ were substituted with LOQ/2 for percentage calculation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

gas phase. Under these conditions, gaseous dry deposition onto vegetation is likely to be the dominant removal pathway, confirming the role of plant cover as a temporary sorptive compartment for light PAHs. This supports the hypothesis that, by the end of the vegetative season, a substantial fraction of accumulated PAHs is transferred to soil via litterfall, contributing to long-term atmospheric removal.

In contrast, winter is characterised by a relative decrease in gaseous LMW PAHs and a concurrent increase in intermediate- and HMW compounds, which are predominantly associated with particulate matter. This pattern reflects lower temperatures, enhanced combustion emissions, atmospheric stability, and precipitation events. These factors favour particle formation and deposition processes, promoting the accumulation of heavier PAHs in terrestrial and aquatic ecosystems.

In this context, temperature plays a crucial role in regulating the partitioning of PAHs between air and plants. Experimental evidence shows that air/plant partition coefficients are exponentially proportional to the inverse of temperature, which is consistent with thermodynamic expectations. Lower temperatures enhance sorption to leaf tissues and increase retention efficiency, whereas higher temperatures promote volatilization and reduce accumulation (Zhao et al., 2018).

The wide range observed for 5 - 6 ring PAHs may reflect differences in traffic intensity, combustion sources, or microclimatic conditions, with local sources or long-range transport potentially influencing the situation in Lascari. Previous studies have shown that PAH partitioning between vegetation and the atmosphere during the growing season is primarily governed by gaseous-phase concentration and temperature (Gao and Zhu, 2004). Models indicate that approximately 44% of PAHs emitted into the atmosphere may be removed by vegetation, based on mass-balance estimates at the regional scale (Simonich and Hites, 1994). Most of the PAHs that are absorbed are likely to be transferred to the soil at the end of the vegetative season, representing a pathway for long-term atmospheric removal (Simonich and Hites, 1994).

In general, the composition of the PAH contamination profile in a given matrix varies according to the emission sources. In the present study, this estimation was carried out using diagnostic distribution indices based on the concentration ratios of selected PAHs (see Table 1). Table 2 reports the calculated ratios, with petrogenic sources highlighted in yellow, mixed sources in orange and pyrogenic emissions in red, for samples collected over the two seasons. These ratios were computed only for samples in which both compounds forming the ratio were quantifiable. Concentrations below the detection limit were not replaced with fractions of the LOD to avoid introducing artifacts in source interpretation.

The results regarding PAH sources suggest that most of the PAHs detected in *C. setaceus* originate from combustion processes, particularly vehicular traffic. Low-molecular-weight PAHs with a molecular mass of 178 and 202 u are often used to distinguish between sources of combustion and petroleum (Yunker et al., 2002; Orecchio, 2007; Orecchio et al., 2022). However, these PAH ratios are influenced by primary sources and vary depending on whether they are transported in the gas phase or absorbed onto primary and secondary aerosols. Photolytic degradation during transport can further alter PAH distribution patterns (Yunker et al., 2002).

It should be noted that the interpretation of PAH diagnostic ratios in plant matrices may be influenced by matrix-specific processes and environmental conditions. Therefore, these ratios should be considered as indicative tools for source identification. Nevertheless, they may provide a useful reference framework for future monitoring of PAH contamination.

In this study, the anthracene/phenanthrene ratio was less than 0.1 in both summer and winter, indicating low-temperature (petrogenic) sources. Phenanthrene is thermodynamically more stable than anthracene, so it is generally present in low concentrations in petrogenic PAHs. In contrast, high-temperature combustion favours the formation of anthracene, thereby increasing the ratio (Yunker et al., 2002). Further source discrimination can be achieved using isomeric ratios, such as Fl/(Fl + Py), which include both gas-phase and particle-associated PAHs. These compounds have comparable physicochemical properties, such as boiling point, vapour pressure, photo-oxidation and partitioning coefficients between air/plant and air/soil. Ratios greater than 0.5 in summer suggest biomass combustion sources, potentially due to an increase in wildfires in the Palermo area. In winter, the ratios ranged from 0.41 to 0.58. Two sites (Casteldaccia and Lascari) exhibited ratios that exceeded 0.5, indicating a mixture of sources, including the combustion of grass, wood, and coal (greater than 0.5), as well as the combustion of gasoline, diesel, and fuel oil (0.4–0.5), which is associated with traffic emissions (Lehndorff and Schwark, 2004).

Winter PAH sources at Lascari and Casteldaccia may also include domestic heating, solid-fuel stoves, charcoal cooking, and local agricultural practices. Other sites with higher vehicular traffic, except for Santa Flavia (a less frequented coastal site in winter), are likely to experience this pollution source. High-molecular-weight PAHs (228 and 276 u) are rarely used as source indicators due to their origin from both petrogenic and pyrogenic emissions.

BA/(BA + Cy) ratios ranged from 0.22 to 0.38 in summer and from 0.29 to 0.42 in winter, indicating a stronger influence of traffic and domestic combustion sources during both seasons. This pattern may reflect traffic-related pollution with secondary contributions from mixed sources and potential photochemical alteration of isomeric ratios.

In summer, I/(I + B) ratios ranged from 0.27 to 0.29 (within the 0.20 - 0.50 range), which is indicative of fossil fuel combustion, primarily from vehicles. In winter, however, I/(I + B) ratios showed greater

Table 2
Isomeric ratios of PAHs in *C. setaceus* collected in August and December from the following sites: 1 = Via Mongerbino; 2 = Viale Regione Siciliana; 3 = Corso Calatafimi; 4 = Via del Vespro; 5 = Via Buonriposo; 6 = Via Salvatore Cappello; 7 = Via Messina Marine; 8 = Via Antonino Laudicina; 9 = Piazza Figurella; 10 = Santa Flavia; 11 = Casteldaccia; 12 = Lascari.

August sampling – isomeric ratios of PAHs in *C. setaceus* samples												
Ratio	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
A/(A+P)				0.077		0.072	0.033	0.097				
Fl/(Fl+Py)	0.676		0.567	0.590	0.638	0.626	0.737	0.555	0.678	0.684	0.615	0.575
BA/(BA+Cy)		0.360	0.298	0.384	0.243		0.364	0.319			0.242	0.223
I/(I+B)				0.292	0.274							
December sampling – isomeric ratios of PAHs in *C. setaceus* samples												
Ratio	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
A/(A+P)	0.084	0.065	0.071	0.097	0.071	0.040		0.097		0.079		
Fl/(Fl+Py)	0.464	0.437	0.427	0.451	0.414	0.500	0.459	0.492	0.477		0.578	0.518
BA/(BA+Cy)	0.317	0.423	0.291	0.363	0.271	0.321	0.306	0.339	0.336		0.356	
I/(I+B)		0.385	0.587	0.575	0.422	0.416						

variability. In sites such as Corso Calatafimi and Via del Vespro, for example, ratios greater than 0.50 indicated significant contributions from biomass and coal combustion, whereas in other sites, the ratios were in the range of 0.38 - 0.42, suggesting a mixture of traffic and domestic combustion sources. Similar results were obtained by Ianiri et al. (2024) for the Palermo sites, suggesting that combustion processes significantly contribute to PAH pollution.

The high variability in PAH concentrations observed in *C. setaceus* samples reflects pronounced pollution gradients, which are driven by emission source intensity and atmospheric dispersion dynamics. Notably, the relative contribution of carcinogenic PAHs to the total PAH burden was higher in urban areas than in coastal or rural sites, emphasizing the stronger impact of traffic-related and combustion-derived inputs in densely populated areas.

While several studies have focused on *Pennisetum* (Zhang et al., 2024), none of these have addressed PAH biomonitoring. Recent research has explored the use of this genus as a bioaccumulator for organic microcontaminants (de Melo et al., 2022) and heavy metals (Hong et al., 2025). These studies have demonstrated the promising bioaccumulation potential of the genus for phytoremediation applications (de Melo et al., 2022; Hong et al., 2025). These findings are relevant both for interpreting bioaccumulation data and for the potential use of the species as a bioindicator. Nevertheless, due to the lack of previous research analysing PAHs in this species, despite the significant spatial and seasonal variability in contamination, it was deemed appropriate to compare the results obtained with data from other plant species.

Özen et al. (2017) reported ΣPAHs in *Alisma plantago-aquatica* from 183 to 798 ng g^{-1} dry weight (d.w.), with higher levels near urban centres and highways, and lower levels at remote sites. A similar spatial pattern was observed in our study, with urban locations showing higher contamination than coastal or less impacted areas.

A more direct comparison can be made with the summer campaign conducted by Ianiri et al. (2024), who sampled *Malva sylvestris* leaves between June and September 2023 at the following five sites: Rotello (rural, Molise), Rome (urban and background) and Palermo (urban and background). During this summer period, the total concentration of PAHs reached 70.2 μg kg^{-1} w.w. at the urban site in Rome, 61.2 μg kg^{-1} w.w. at the urban site in Palermo, and 100.0 μg kg^{-1} w.w. at the Palermo background site, while all compounds were below detection limits at the rural site of Rotello and at the background site in Rome.

In our study, the median Σ16 PAHs concentration in August was 102 μg kg^{-1} w.w., ranging from 86.2 to 254 μg kg^{-1} w.w. Therefore, the summer levels observed in *C. setaceus* are comparable to or higher than those reported by Ianiri et al. (2024) for *M. sylvestris* during the same season, particularly at the urban sites in Rome and Palermo.

Culotta et al. (2005) found 19 PAHs in *Nerium oleander* leaves in Palermo from 10 to 166 μg kg^{-1} d.w., with urban sites showing higher concentrations. It is important to note that Culotta et al. (2005) conducted their campaign in winter, approximately twenty years before the present work, and sampled sites that were generally different from those considered here.

Despite these differences, the pattern of dominant compounds (fluoranthene, pyrene, and phenanthrene) was consistent with our December campaign, although Σ16 PAHs in *C. setaceus* reached higher values, likely reflecting differences in sampling sites and periods, as well as the species greater accumulation capacity.

Similar trends were observed in herbaceous species, including *Poaceae*, in eastern China where Σ16 PAHs ranged from 123 to 743 ng g^{-1} w.w. with mean and median values of 274.66 and 234 ng g^{-1}, respectively (Zhao et al., 2022). In the present study, summer levels of Σ16 PAH in *C. setaceus* are lower than the average reported for Chinese plants, but within the observed range. Instead, winter concentrations show a median value that is very close to that of herbaceous species (218 vs. 234 ng g^{-1}), and they exceed the maximum values recorded at the most impacted sites (1217 vs 743 ng g^{-1}).

In both studies, plant tissues mainly contained LMW and IMW PAHs, with source diagnostics pointing to a pyrogenic origin. The ability of some *Poaceae* species to accumulate PAHs supports comparison with *C. setaceus*, suggesting that this invasive species could serve as a reliable bioindicator and aid phytoremediation.

Between April and July 2008, Sojinu et al. (2010) collected leaves from 11 higher plant species at a moderately polluted site in Nigeria. They reported high PAH accumulation in these plants on a dry weight basis, with Σ28 PAHs ranging from 365 to 2870 ng g^{-1} d.w. with an average of 1430 ng g^{-1} d.w. The profile was dominated by 2- and 3-ring PAHs, while 4–6 ring compounds were less abundant. Among the *Poaceae*, *Pennisetum purpureum* exhibited the highest concentrations consistently. To enable a semi-direct comparison with our study, only the 16 PAHs common to both datasets were considered. The sum of the 16 PAHs in *P. purpureum* ranged from 164 to 1235 μg/kg d.w., confirming its strong accumulation potential. It should be noted that, as these concentrations are expressed on a dry weight basis, the corresponding wet weight levels would be lower.

The PAHs levels in *P. purpureum* were comparable to those observed in *C. setaceus*, suggesting its potential as a biomonitor of PAHs pollution. However, differences in the sampling period, seasonal deposition, local emission patterns and site-specific pollution sources likely influenced the observed concentrations.

A comparison with literature data for other plant species indicates that the PAH concentrations are of a similar magnitude, and in some cases even higher. This supports the suitability of *C. setaceus* as an effective passive collector of atmospheric PAHs contamination. These findings suggest that this species can reliably reflect spatial differences in air quality and pollutant sources.

Furthermore, preserved plant samples could enable retrospective PAH analyses if collection and storage procedures are standardised over time. In this way, archived biomass could serve as a reliable record of temporal variations in PAH concentrations within this biological matrix.

From a complementary perspective, this species' potential for phytoremediation deserves consideration. While its spread raises ecological concerns due to the displacement of endemic or native flora, other species of the same genus have demonstrated tolerance and sustained growth under elevated PAH concentrations (Koul and Fulekar, 2016). This suggests a potential role in the progressive attenuation of hydrocarbon pollution over time.

Within this framework, management and eradication strategies could provide multiple environmental benefits, including controlling the spread of this invasive species, exploiting its temporary role in contaminant retention, evaluating the potential for valorising harvested biomass and obtaining detailed information on local pollution through the chemical characterisation of plant tissues prior to disposal. Continued research on biomonitoring additional pollutants, together with studies on the species' distribution, ecological impacts and management approaches, is essential to support sustainable control measures and guide future investigations.

4. Conclusion

This study is the first to assess PAHs in *C. setaceus*, an invasive species of Union concern that is expanding its range rapidly. The findings of the investigation highlight the capacity of this species to function as a biomonitor and collector of urban PAHs. The research, conducted in urban and coastal regions of Palermo, has revealed significant spatial and seasonal variations in contamination levels. Summer concentrations were relatively consistent across sites, whereas winter levels exhibited a much wider range, reflecting local emission intensity and meteorological conditions. These seasonal differences are consistent with known physicochemical and biological processes, including enhanced volatilization and photodegradation in summer, and enhanced retention due to lower temperatures, thermal inversions, and particulate deposition during winter.

The distribution of PAHs according to molecular weight showed that LMW compounds dominated in summer, while intermediate- and HMW PAHs increased in winter. This seasonal pattern indicates the critical role of temperature in air/plant partitioning, with gas-phase deposition predominating for lighter compounds and particulate-associated deposition for heavier PAHs. Diagnostic isomeric ratios confirmed that combustion processes, particularly vehicular traffic, are the main source of PAHs, with additional contributions from biomass and domestic heating in specific sites during winter.

Comparisons with literature data demonstrate that PAH accumulation in *C. setaceus* is similar to, or even higher than, that observed in other herbaceous and woody species. Its high accumulation potential, year-round persistence and ease of sampling make *C. setaceus* a practical biomonitoring tool for atmospheric PAHs, providing time-integrated information that complements conventional instrumental techniques.

Compared to traditional monitoring techniques, the analysis of PAHs in *C. setaceus* represents a simple tool for assessing air quality over extended periods. As it persists year-round as an invasive species, it enables continuous biomonitoring without the need for seasonal sampling constraints. While this approach does not replace conventional methods, it complements them by providing integrated, time-averaged information on atmospheric contamination. Its cost-effectiveness and operational simplicity make it particularly suitable for small communities or individuals interested in evaluating local environmental conditions.

Furthermore, preserved plant samples could enable retrospective PAH analyses if collection and storage procedures are standardised over time. In this way, archived biomass could serve as a reliable record of temporal variations in PAH concentrations within this biological matrix.

From a management perspective, this study suggests that this invasive species could play a dual role in urban environments, acting as a passive collector of atmospheric PAHs in urban settings and as a candidate for phytoremediation strategies. Although its management should aim to prevent the further ecological displacement of native flora, the harvested biomass could be analysed to provide local contamination data. Over time, its PAH sequestration capacity could help to reduce hydrocarbon pollution. This approach may also support invasive species management by linking biomass removal to environmental monitoring and potential valorisation of harvested material.

Overall, *C. setaceus* represents a valuable addition to the biomonitoring toolkit, combining operational simplicity, cost-effectiveness and high sensitivity to spatial and seasonal variations in atmospheric PAH levels. Future studies should explore its long-term accumulation patterns, potential for pollutant transfer to soil, and practical applications in urban phytoremediation programs.

CRediT authorship contribution statement

Dario Savoca: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Silvia Orecchio:** Writing – review & editing, Formal analysis, Data curation. **Antonella Maccotta:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Michele Bruno:** Software, Investigation, Formal analysis. **Vincenzo Arizza:** Writing – review & editing, Supervision, Project administration. **Salvatore Barreca:** Visualization, Software, Investigation, Data curation. **Giuseppe Arrabito:** Visualization, Software, Investigation, Data curation. **Diana Amorello:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2026.128279.

Data availability

Data will be made available on request.

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