Tracing historical changes, degradation, and original sources of airborne polycyclic aromatic hydrocarbons (PAHs) in Jilin Province, China, by Abies holophylla and Pinus tabuliformisneedle leaves

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Abstract:

Due to their wide distribution and availability, plant leaves are interesting biomonitoring candidates for the evaluation of atmospheric pollution. In addition, leaves from some species can also retain historical information, for example related to environmental pollution, due to their class age. In this study, the content of polycyclic aromatic hydrocarbons (PAHs) in *Abies holophylla* and *Pinus tabuliformis* needles in function of their class age have been investigated to obtain information regarding the degradation constant for each PAH under investigation, and to evaluate the possibility to correlate the presence of PAHs in needles with some important environmental factors. It has been demonstrated that the total PAH concentration in the needles, for both species, increased proportionally with the age of needles, ranging from 804 to 3604 ng g^{-1} (dry weight), showing a general tendence to accumulate these substances through years, while degradation rates increased with molecular complexity. Finally, a study on the possible correlation between adsorbed PAH contents in needle leaves and pollution emission sources have been carried out, demonstrating that this biomonitoring system could be fruitfully used to trace historical changes and original sources of airborne PAHs.

Keywords: Polycyclic aromatic hydrocarbons (PAHs); Air pollution biomonitoring; PAH degradation constants; *Abies holophylla*; *Pinus tabuliformis*

1. Introduction

The determination of polycyclic aromatic hydrocarbons (PAHs) level caused by air pollution is one of the problems of major concern in recent decades. Airborne PAHs are produced by incomplete combustion of industrial emissions and transportation (Chang et al., 2006; Rodgman et al., 2000), as well as wildfire (Choi, 2014; Lao et al., 2018), and their monitoring has been considered a challenging and important activity, due to the carcinogenic, mutagenic, and teratogenic effects of these substances on human health. PAHs determination anyway could encounter technical, physical, and economical limitations when active air samplers are used, while sampling tree components like needles, leaves and barks, suitable for the determination of the spatial distribution of PAHs, are usually employed only to measure the current levels of atmospheric PAHs (Amigo et al., 2011; De Nicola et al., 2011; Zhou et al., 2014). Recent studies on the historical record of PAHs have been conducted in the growth rings, lake sediments and ice cores of specific areas (Cai et al., 2016; Kuang et al., 2015; Wang et al., 2008), but these sampling sites impose several constrains, limiting the monitoring to specific conditions in terms of spatial recognition and time intervals.

Plants can be considered a very interesting and advantageous biomonitoring substrate in particular for PAHs, due to the hydrophobic lipid layers that can retain these substances (Kim et al., 2014; Paterson et al., 1991). For example, it has been demonstrated that diffusive uptake and storage function of polymeric lipids of plants play a key role in the transport and fate of phenanthrene (Li and Chen, 2014). A unique and very useful characteristic of conifer needles is that they can grow up and last for several years, thus preserving the history of the environmental conditions. Furthermore, some PAHs can be used as a marker of certain pollution sources: for example, it was found that the prevalence of lower molecular weight compounds in ambient air samples can be essentially related to the road traffic, more specifically with vehicles of diesel engines (Albuquerque et al., 2016). There have also been variation studies using some specific PAH content ratio in needles, such as Ant/(Ant + Phen) or Flt/(Flt + Pyr), to identify local sources of contamination (Esen et al., 2008; Galarneau, 2008; Kong et al.,

2015).

On the base of these considerations, *Abies holophylla* needles from 1 to 6 years old (2016-2011) old and *Pinus tabuliformis* from 1 to 4 years old (2015-2012) have been collected to investigate the species-specificity historical variations of PAHs and to investigate the possible relation between emitted air pollutants and PAHs in the needles over the years, also taking into account the PAH degradation into the needle leaves. To pursue this target a mathematical model to interpret the PAH degradation has been proposed. Finally, PAHs content in conifer needles were correlated with pollutant sources of airborne PAHs throughout the studied years.

2. Material and methods

2.1 Materials and standards

Standard mixtures of 16 PAHs (naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd] pyrene (IcdP), dibenzo[a,h]anthracene (DahA) and benzo[ghi]perylene (BghiP)) and 3 deuterated PAHs (Phenanthrene-d_8, Fluoranthene-d_{12} and Perylene-d_{12}) were purchased from Sigma Aldrich (St. Louis, MO, USA). The purity of all standards was up to 98%. Silica (100-200 mesh) and Al_2O_3 adsorbent was obtained from Sigma Aldrich (St. Louis, MO, USA). To remove the contaminants, all adsorbents and glasswares were heated at 400°C for 12 h.

2.2 Sampling and processing

Two plant species with 4 years and 6 years old needles were selected for this study. Needles from 1 (2016) to 6 years (2011) and from 1 (2015) to 4 years (2012) old were collected from *Abies holophylla* and *Pinus tabuliformis*, respectively. Age of needles was evaluated by growth ring and branching pattern, and it was confirmed in combination with the situation at the branch cut (**Fig. 1**) (Pérez-Harguindeguy et al., 2013). During collection, in order to ensure a better

98 authenticity and accuracy, needles of the same year at the upper 1/3 and lower 1/3 of the canopy
99 of tree species were mixed into one sample, cleaned, freeze-dried, crushed by 200 mesh, and
100 stored at -20°C for further analysis.

101

102 **Fig. 1.** Photographs that show the branch information of A) *Abies holophylla*, and the growth
103 ring patterns of B) *Abies holophylla* and C) *Pinus tabuliformis*.

104 Eleven air pollutant emission variables with an expected environmental impact on the
105 concentrations of PAHs, namely coal (Ton year^{-1}), crude oil (Ton year^{-1}), and electricity (MKh
106 year^{-1}) consumption; number of civil vehicles and trucks (Unit year^{-1}); emission of industrial
107 sulfur, nitrogen oxide, industrial smoke (dust), and soot (Ton year^{-1}); urban living gaseous
108 pollutant emissions (Ton year^{-1}); generating capacity (KWh year^{-1}) were obtained for the
109 interested areas from the databases of the China National Statistics Institute ("SBJ (Statistic
110 bureau of Jilin-Statistics China)," 2016).

111 **2.3 Measurement of lipid content**

112 Needle lipid contents were measured as follows: 3 g of dry needles were extracted 3 times
113 using ultrasonication with 20 mL n-hexane:acetone (50:50, v:v) for 20 min each. The extract
114 was concentrated, dried and finally weighed to calculate the lipid content (Zhao et al., 2018).

2.4 PAHs analysis

2.4.1 Extraction of PAHs

All the samples were spiked using internal standards. The sample pre-treatment procedures were performed according to the method in our previous publication with slight modification (Jin et al., 2020). In brief, a total of 0.5 g homogenized, crushed and sieved needles powder was spiked with internal standards, then mixed with 10 mL of dichloromethane (DCM) and ultrasonically extracted 3 times per 15 min. The combined extract was replaced with n-hexane and concentrated to 0.5 mL prior to SPE clean up. The SPE column (down-top: 2.0 g Na_2SO_4, 1.5 g silica gel, 0.8 g Al_2O_3 (deactivated with 2% ultrapure water), and 4.0 g Na_2SO_4) was conditioned with n-hexane before sample loading. It was eluted with 3 mL n-hexane (discarded) followed by 9 mL n-hexane/DCM (1:1, v/v) (first 3 mL was discarded). The 6 mL eluted extract was concentrated via a gentle stream of nitrogen gas at room temperature, and reconstituted with 100 μL of n-hexane. Then, gas purge microsyringe extraction (GP-MSE) was used for further purification, as described in a previous work (Yang et al., 2011), and the final volume was adjusted to 100 μL. Finally, 2 μL of the purified extract was injected to the GC-MS system for analysis.

2.4.2 GC-MS analysis

PAHs were analyzed quantitatively and qualitatively by Shimadzu gas chromatograph equipped with DB-5MS fused silica capillary column (30 m × 0.25 mm; thickness: 0.25 μm, Restek Corporation, Bellefonte, PA, USA) and QPMS 2010 mass spectrometry detector. The conditions for GC-MS analysis were as follows: sample injection was carried out in splitless mode at 280°C, using He as a carrier gas at a flow rate of 1 ml min^{-1}. GC-MS interface temperature was set at 280°C, ionization voltage was 70 eV and ion source temperature was set at 200°C. The initial oven temperature was held at 80°C for 1 min, then was brought to 100°C at the rate of 20°C min^{-1}, from 100°C to 200°C at 10°C min^{-1} and 200°C to 280°C at 20°C min^{-1}, holding this last value for 2 min. Data was collected in selected ion monitoring mode (SIM).

The relative percentage difference for individual PAH determined in paired duplicate samples (n = 2) was always < 24%. The obtained recovery for all the PAHs was between 64 and 120% with respect to the certified values.

3. Results and discussion

3.1 Adsorbed PAHs in needles

Usually, PAHs content in plant samples is normalized by lipid content or dry weight. Studies have shown that both cuticle and suberin (a cell wall component) may act as lipids in different parts of the plant, but they are not solvent extractable (Chen et al., 2012; Ockenden et al., 1998; Taiz and Zeiger, 2010). For this reason, the needle lipid content obtained by the classical method may not reflect the total amount of substances acting as PAH extracting lipids. The total measured extractable PAH concentrations found in this work are given in **Table 1**. The needle lipid contents in *Abies holophylla* and *Pinus tabuliformis* ranged from 27.46 to 32.16%, and from 6.85 to 9.56% (respect to dry weight), respectively. By comparing the total extractable PAH concentrations with lipid contents of needles, no significant correlation was found (R = -0.12 - 0.646, p > 0.354). Hence PAHs contents were expressed on a dry weight basis in this study.

Table 1 Temporal trends of PAH total contents recorded in needles of *Abies holophylla* and *Pinus tabuliformis*.

Rings	***Abies holophylla* (ng g^{-1})**					
	2016	**2015**	**2014**	**2013**	**2012**	**2011**
2	43 ± 2	52 ± 17	42 ± 5	38 ± 1	38 ± 2	45 ± 7
3	981 ± 76	1503 ± 10	1669 ± 13	1820 ± 82	2135 ± 149	2340 ± 34
4	438 ± 133	588 ± 98	762 ± 204	815 ± 158	893 ± 84	1228 ± 130
5,6	18 ± 1	14 ± 1	9 ± 2	16 ± 2	10 ± 4	21 ± 7
Total PAHs	1449 ± 212	2113 ± 106	2446 ± 189	2663 ± 73	3044 ± 67	3604 ± 96

Rings	***Pinus tabuliformis* (ng g^{-1})**			
	2015	**2014**	**2013**	**2012**

2	119 ± 4	100 ± 1	105 ± 25	72 ± 8
3	498 ± 112	829 ± 102	845 ± 66	910 ± 39
4	152 ± 10	241 ± 22	319 ± 51	308 ± 30
5,6	34 ± 7	28 ± 3	65 ± 39	145 ± 77
Total PAHs	804 ± 99	1197 ± 127	1334 ± 131	1435 ± 93

As expected, due to the accumulating effect, PAH contents generally increase with the needles age, accordingly to the results obtained by previous works (Odabasi et al., 2015; Ratola et al., 2010a). Furthermore, *Abies holophylla* needles generally showed a higher tendence to accumulate PAHs in respect to *Pinus tabuliformis* needles. The concentration of 3-4 ring PAHs increase over time, and this result is consistent with a previous work (Ratola et al., 2010a). These values were found to be higher than 5-6 ring PAHs, which are in good agreement with the accumulation pattern of PAHs in needles of other pine species, including *Pinus halepensis* and *P. pinea* (Librando et al., 2002), *Pinus pinaster* and *Pinus nigra* (Piccardo et al., 2005) and *P. pinaster* and *P. pinea* (Ratola et al., 2010a). Because of the volatile nature of Naph (2 ring), its fast photodegradation process and re-suspension capability leads to a non-stable accumulation in the needles (Choi, 2014; Wang et al., 2005). Lighter PAHs (3-4 ring), which are predominantly present in the gaseous phase, interact strongly with the waxy layer of the needles and this effect can promote PAH uptakes in needles (Lehndorff and Schwark, 2004). The low content of heavier PAHs (5-6 rings) observed in this work confirms what already noticed in previous works, and it could be related to the fact that their adsorption in needle leaves can be hindered by their different distribution in the environment. These PAHs are present in fact preferentially in the particulate phase of the atmosphere, and for this reason their migration from atmosphere can be slower if compared with other PAHs (Yang et al., 2017). The accumulation process may vary from species to species, leading to different concentration in needles (Ratola et al., 2011). This behavior has been noticed also for the species in this work, even if a similar PAH trend for years 1 to 4 with *Abies holophylla* and *Pinus tabuliformis* needles were noticed. More than 64 % of adsorbed PAHs in the needles are composed of 3-4 rings: this value roughly reflects PAH composition in the air in both urban and industrial areas (Li et al., 2016; Odabasi et al., 2015; Tomashuk et al., 2012).

3.2 A study on PAH degradation constants in *Abies holophylla* needles

As already pointed out, PAHs are present in gas and particle phases of the atmosphere and diffuse into plant leaves through dry and wet deposition. Their sources are closely related to the anthropogenic combustion processes (e.g. car exhaust, local heating facilities, industrial related activities). It has been already demonstrated that the PAH degradation follows a first-order kinetics (Haritash and Kaushik, 2009), even if dependent from external variables: for example, fly ash and carbon black, that can protect PAHs from photo decomposition (Behymer and Hites, 1985; Korfmacher et al., 1980). Anyway, in principle the PAH amount collected in different years by needles undergo through a degradation mechanism that follows an exponential trend, which can be described by these equations:

$$C_{year}^{Tot} = \sum_{i=0}^{n} C_i e^{-\alpha t_i} \qquad \text{Eq.1}$$

Where C_{year}^{Tot} is the content (obtained experimentally) for each PAH, C_i is the PAH amount that can be attributed to a specific year, α is the degradation kinetic constant and t_i is the time expressed in years. This model was then applied to PAH contents in *Abies holophylla* needles, considering that for this species data were collected from 2011 to 2016, a longer period if compared to data obtained by *Pinus tabuliformis*. In this case, it is possible to write for each year the following equations:

$$C_{2011}^{Tot} = C_{\leq 2010} e^{-\alpha} + C_{2011} \qquad \text{Eq.2}$$

$$C_{2012}^{Tot} = C_{\leq 2010} e^{-2\alpha} + C_{2011} e^{-\alpha} + C_{2012} \qquad \text{Eq.3}$$

$$C_{2013}^{Tot} = C_{\leq 2010} e^{-3\alpha} + C_{2011} e^{-2\alpha} + C_{2012} e^{-\alpha} + C_{2013} \qquad \text{Eq.4}$$

$$C_{2014}^{Tot} = C_{\leq 2010} e^{-4\alpha} + C_{2011} e^{-3\alpha} + C_{2012} e^{-2\alpha} + C_{2013} e^{-\alpha} + C_{2014} \qquad \text{Eq.5}$$

$$C_{2015}^{Tot} = C_{\leq 2010} e^{-5\alpha} + C_{2011} e^{-4\alpha} + C_{2012} e^{-3\alpha} + C_{2013} e^{-2\alpha} + C_{2014} e^{-\alpha} + C_{2015} \qquad \text{Eq.6}$$

$$C_{2016}^{Tot} = C_{\leq 2010} e^{-6\alpha} + C_{2011} e^{-5\alpha} + C_{2012} e^{-4\alpha} + C_{2013} e^{-3\alpha} + C_{2014} e^{-2\alpha} + C_{2015} e^{-\alpha} + C_{2016} \qquad \text{Eq.7}$$

200 Considering $e^{-\alpha t} = y$ we have:

$$C_{2011}^{Tot} = C_{\leq 2010} y + C_{2011} \quad \text{Eq.8}$$

$$C_{2012}^{Tot} = C_{\leq 2010} y^2 + C_{2011} y + C_{2012} = (C_{\leq 2010} y + C_{2011}) y + C_{2012} = C_{2011}^{Tot} y + C_{2012} \quad \text{Eq.9}$$

201 and then, applying the same elaboration to other years:

$$C_{2013}^{Tot} = C_{2012}^{Tot} y + C_{2013} \quad \text{Eq.10}$$

$$C_{2014}^{Tot} = C_{2013}^{Tot} y + C_{2014} \quad \text{Eq.11}$$

$$C_{2015}^{Tot} = C_{2014}^{Tot} y + C_{2015} \quad \text{Eq.12}$$

$$C_{2016}^{Tot} = C_{2015}^{Tot} y + C_{2016} \quad \text{Eq.13}$$

202 On the base of **Eq. 9-13**, considering that C_{year} and y should be always ≥ 0, it is possible
203 to individuate the minimum acceptable α values and the relevant minimum PAH degradation
204 percentage per year (**Table 2**). To our knowledge, no studies have been carried out regarding
205 the PAH degradation in leaves. Cutright (Cutright, 1995) reported a study to determine the
206 specific degradation rates for the bioremediation of PAH-contaminated soils. Other studies
207 demonstrated that the degradation rate of high molecular weight PAHs is slower than other
208 PAHs (Johnsen et al., 2005), and as an important factor for the PAH-degradation activity, of the
209 pH changes by the bacteria could be the reason (Kästner et al., 1998).

210 **Table 2** Minimum percentage of PAH degradation year^{-1} and minimum values of the
211 degradation constant.

Rings	Compound	Minimum degradation per year (%)	Minimum *a* value
2	Naph	32	0.387
3	Acy	16	0.173
3	Ace	34	0.421
3	Fluo	39	0.501
3	Phen	27	0.309
3	Ant	41	0.533
3	Flt	35	0.428

4	Pyr	35	0.423
4	BaA	39	0.496
4	Chry	32	0.382
4	BbF	35	0.434
4	BkF	62	0.962
4	BaP	25	0.987
5	IcdP	81	1.681
5	DahA	85	1.870
6	BghiP	81	1.647

On the contrary, in this study it is interesting to note that higher is the number of rings (i.e. IcdP, DahA and BghiP), higher is the degradation constant, with the consequence of high degradation rates. This different behavior is most probably due to the fact that degradation rates in soil are governed by bacteria activity (Roslund et al., 2018), which is not present in the needles where decomposition is mostly dependent on PAH chemical stability. The proposed degradation model allows an estimation of the PAH contents retained by needles every year. In **Fig. 2**, the normalized PAH contents in needle are displayed. 3 and 4 rings PAHs show a decrease from 2011 to 2016, while for 2 and 5-6 rings PAHs the behavior seems not following any particular trend.

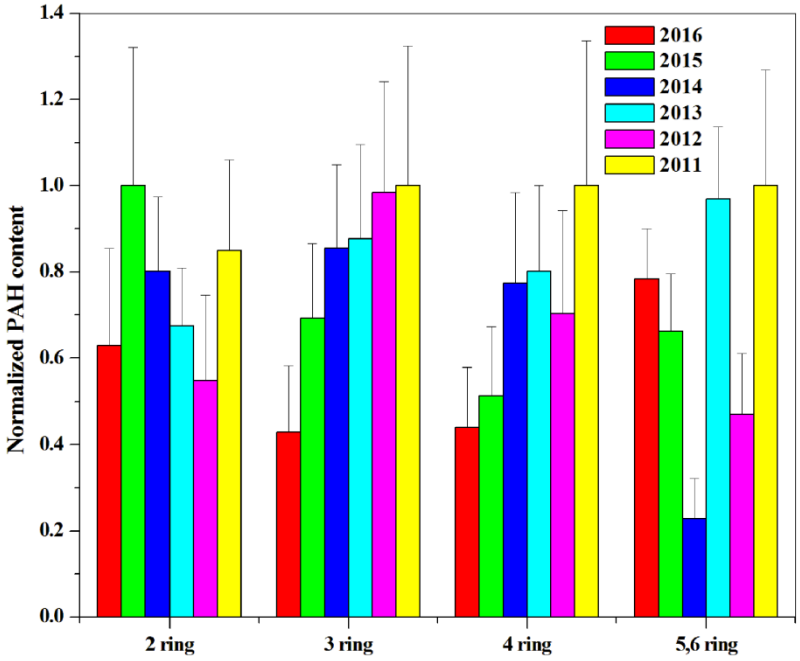


Fig. 2. Normalized PAH content differentiated by the number of rings, in function of different

223 years. Error bars represent standard deviations.

224 ### 3.3 Correlation between adsorbed PAHs in *Abies holophylla* needles and air pollutant
225 emission variables in needles

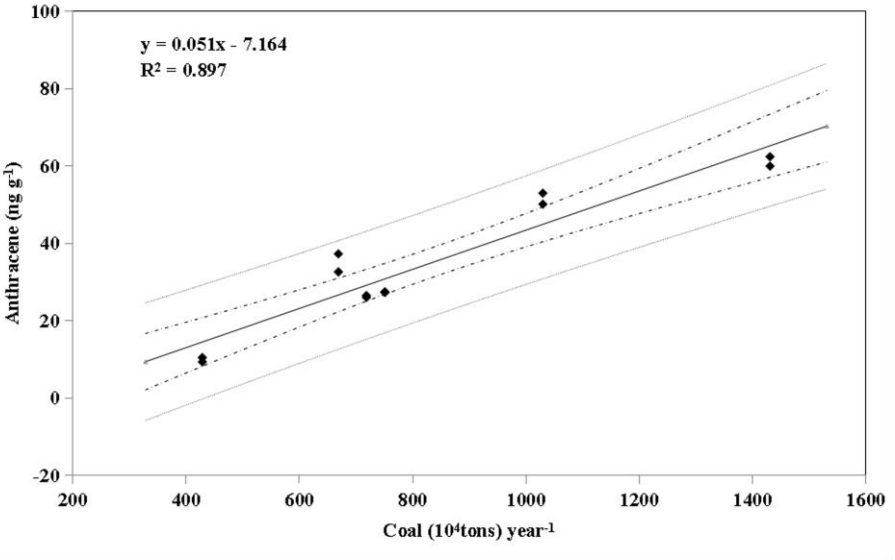
226 PAHs sources are closely related to the anthropogenic combustion processes (e.g. car
227 exhaust, local heating facilities, industrial related activities). For this reason, it could be
228 hypothesized a correlation between adsorbed PAHs and some air pollutant emission parameters.
229 From China National Statistics Institute, it is possible to obtain data concerning: annual
230 consumption of coal (Ton year^{-1}), crude oil (Ton year^{-1}) and electricity (MKh year^{-1})
231 consumption; number of civil vehicles and trucks (Unit year^{-1}); emission of industrial sulfur,
232 nitrogen oxide, industrial smoke (dust), and soot (Ton year^{-1}); urban living gaseous pollutant
233 emissions (Ton year^{-1}); generating capacity (KWh year^{-1}). Correlation coefficients were then
234 obtained considering these parameters and PAHs average values from *Abies holophylla*.

235 **Table 3** Correlation coefficients (R) between air pollution parameters and the average values
236 of adsorbed PAHs obtained from *Abies holophylla*. Only R > 0.8 values are displayed.

Air pollutant parameter	PAH	Correlation coefficient(R)
Coal	Fluo	0.817
	Phen	0.947
	Ant	0.874
Electricity	Flt	0.915
	Pyr	0.925
	BaA	0.906
	Chry	0.947
Trucks	BbF	0.814
Industrial sulfur emissions	Fluo	0.862
	Phen	0.857
	Acy	0.869
	Ace	0.982
Industrial nitrogen oxide emissions	Fluo	0.956
	Phen	0.934
	Ant	0.848
	Flt	0.908

Vehicle number	Pyr	0.833
	BaP	0.888
Industrial gaseous pollutant emissions	Ace	0.816
	Fluo	0.866
	Phen	0.864
Generating capacity	Flt	0.915
	Pyr	0.925
	BaA	0.911
	Chry	0.947

The concentration of PAH congener shows good correlation with meteorological parameters (**Table 3**). For example, **Fig. 3** shows a typical correlation graph obtained between coal consumption per year and Ant contents in needle. Several interesting considerations can be made based on Table 3. For instance, Fluo, Phen and Ant are well correlated with coal consumption, and this correlation can be ascribed to their production during combustion (Dameng et al., 2011). In particular, in this last process, Phen production is the highest when compared to the PAHs investigated in this work, and this could lead to the very high correlation value (0.947). On the other hand, these three PAHs are not the only ones produced during coal combustion, but, most probably, the lack in correlation could be due to other interfering processes. The correlation existing between the number of trucks and BbF can be ascribed to its production by diesel engines (Kuusimäki et al., 2002). It is also worth to note the high number of PAH that are correlated with industrial nitrogen oxide emissions, suggesting that NOx production can be strongly related to the emission of these PAHs in the atmosphere.



250

251 **Fig. 3.** A graph showing the correlations between coal consumption per year and anthracene
252 content in *Abies holophylla* leaves. The solid line and dotted line curves represent
253 confidence limits for the prediction and confidence limits for the regression line at
254 95% confidence level, respectively.

255 In the urban areas, traffic emission is the dominant source of PAHs (Ratola et al., 2010b),
256 in particular 3-4 rings PAHs: this could explain the good correlation between vehicle number
257 and BaP. Surprisingly, none of the 5 and 6 ring PAHs shows correlation with any of the pollution
258 sources, probably because of their fast degradation constant ($\alpha \geq 1.65$) that does not allow to
259 recover time dependent information from needles, and due to the molecule dimensions that
260 make it more difficult to be adsorbed onto pine needles (Yang et al., 2007).

261 **4. Conclusions**

262 In this study, the possibility to evaluate PAH historical changes and their correlation with
263 pollution emission sources by PAH contents in the needles of *Abies holophylla* and *Pinus*
264 *tabuliformis* has been investigated. Using the PAH content in *Abies holophylla* needles, a
265 mathematical model that consider a first order PAH degradation process has been applied in
266 order to obtain the minimum degradation per year and the minimum α value for each of the
267 considered PAH. Results indicate that higher is the number of rings (i.e. IcdP and DahA and

BghiP), higher is the degradation constant in the needles, with the consequence of high degradation rates. Furthermore, considering that PAHs sources are closely related to the anthropogenic pollution processes, the adsorbed PAHs content calculated by the mathematical model from 2011 to 2016 in *Abies holophylla* leaves have been statistically compared with air pollutant emission parameters obtained from the databases, obtaining in some cases a good correlation ($R > 0.8$) among data. The obtained results indicate that adsorbed PAHs in needle leaves are good candidate as biomonitoring system to evaluate the historical changes of PAHs induced by pollutant emission on the regional scale.

Conflicts of 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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Declaration of interests

☒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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Sincerely,

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Graphical Abstract (for review)

Highlights

- PAH contents in *Abies holophylla* and *Pinus tabuliformis* needles have been evaluated.
- A mathematical model to calculate PAH degradation in pine needles was developed.
- Degradation constants in needles increased with the number of rings in PAHs.
- Correlations between specific adsorbed PAHs in needle leaves and air pollutant sources was found.

Figure 1

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Figure 2

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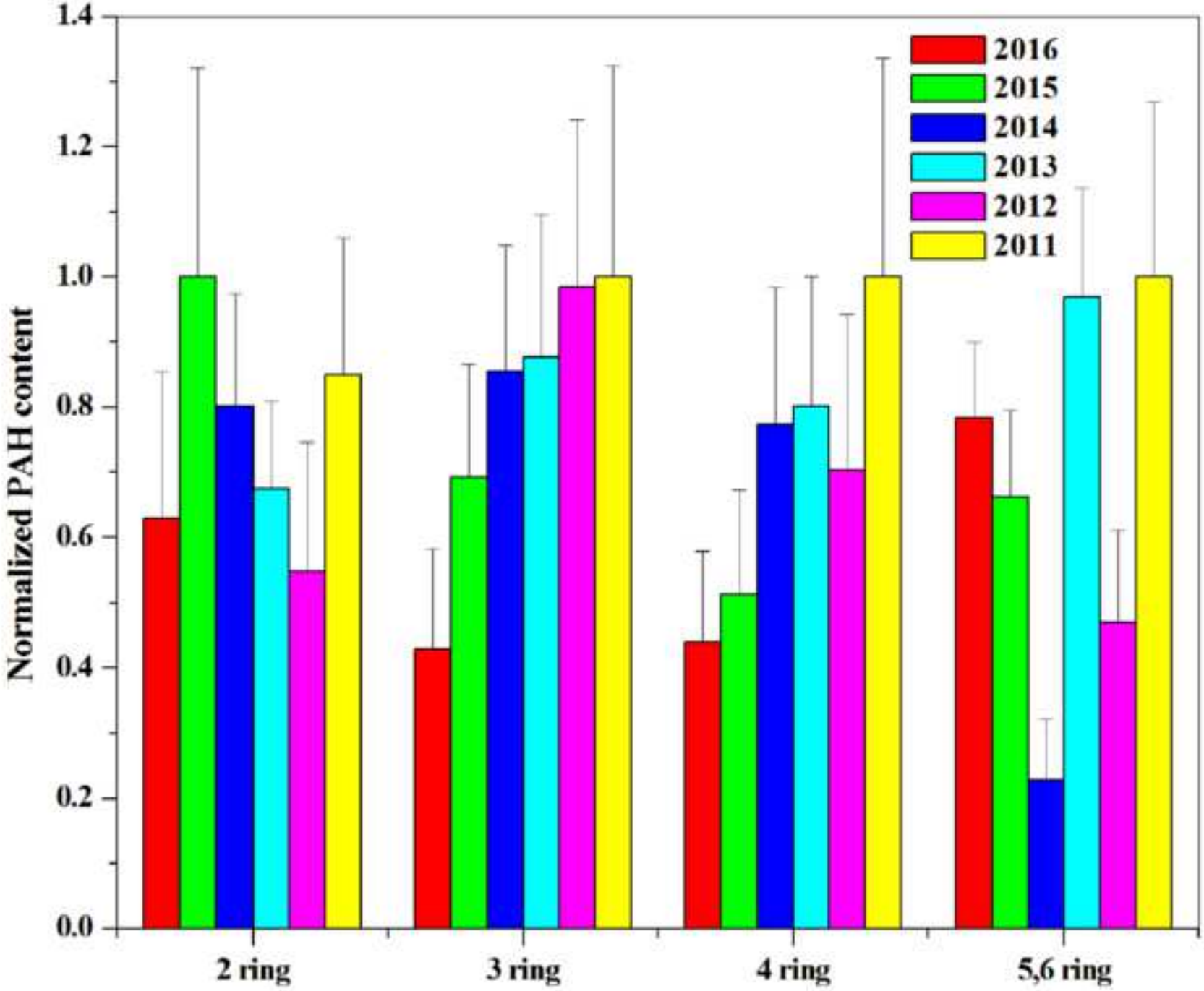

Figure 3

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