

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

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Research Article

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

Posted Date: July 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-269882/v2>

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on August 31st, 2021. See the published version at <https://doi.org/10.1007/s11356-021-16176-4>.

1 **Tracing historical changes, degradation, and original sources of airborne**
2 **polycyclic aromatic hydrocarbons (PAHs) in Jilin Province, China, by *Abies***
3 ***holophylla* and *Pinus tabuliformis* needle leaves**

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22 **Abstract:** Due to their wide distribution and availability, plant leaves can be considered
23 interesting candidates as biomonitoring substrates for the evaluation of atmospheric pollution.
24 In addition, some species can also retain historical information, for example, related to
25 environmental pollution, due to their leaf class age. In this study, the content of polycyclic
26 aromatic hydrocarbons (PAHs) in *Abies holophylla* and *Pinus tabuliformis* needle samples in
27 function of their class age has been investigated to obtain information regarding the degradation
28 constant for each PAH under investigation (α values ranging from 0.173 to 1.870) and to
29 evaluate the possibility to correlate the presence of PAHs in needles with some important
30 pollution environmental factors. Considering air pollutant variables registered in Jilin Province,
31 significant correlations (at 95% confidence level) have been found between coal consumption
32 per year and anthracene contents in needles, while fluorene, phenanthrene, and anthracene
33 resulted correlated with coal consumption. Furthermore, it has been demonstrated that the total
34 PAH concentration in needles, for both species, increased with their age (from 804 to 3604 ng
35 g⁻¹ dry weight), showing a general tendency to accumulate these substances through years. PAH
36 degradation rates increased instead with molecular complexity. This study could be considered
37 a first trial to obtain historical environmental information by pine needles biomonitoring.

38

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

41 **1. Introduction**

42 The presence of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere represents
43 one of the problems of major concern related to air pollution in recent decades. Airborne PAHs
44 are produced by incomplete combustion of industrial emissions and transportation (Rodgman
45 et al. 2000; Chang et al. 2006), as well as wildfire (Choi 2014; Lao et al. 2018), and their
46 monitoring has been considered a challenging activity, due to the carcinogenic, mutagenic, and
47 teratogenic effects of these substances on human health (International Agency for Research on
48 Cancer 1983; Hopkins 1989). PAHs determination, anyway, could encounter technical, physical,
49 and economical limitations when active air samplers are used, while sampling tree components
50 like needles, leaves and barks, suitable for the determination of the spatial distribution of PAHs,
51 are usually employed only to measure the current levels of atmospheric PAHs (De Nicola et al.
52 2011; Amigo et al. 2011; Zhou et al. 2014). Recent studies on the historical record of PAHs
53 have been conducted in lake sediments and ice cores of specific areas (Wang et al. 2008; Cai et
54 al. 2016), but these sampling sites impose several constraints, limiting the monitoring to
55 specific conditions in terms of spatial recognition and time intervals.

56 Plants can be considered a very interesting and advantageous biomonitoring substrate in
57 particular for PAH monitoring, due to the hydrophobic lipid layers that can retain these
58 substances (Paterson et al. 1991; Kim et al. 2014). For example, it has been demonstrated that
59 diffusive uptake and storage function of polymeric lipids of plants play a key role in the
60 transport and fate of phenanthrene (Li and Chen 2014). A unique and very useful characteristic
61 of conifer needles is that they can grow up and last for several years, thus preserving the history
62 of the environmental conditions (Navarro–Ortega et al. 2012; Noth et al. 2013; Fernández–
63 Varela et al. 2015). Furthermore, some PAHs can be used as a marker of certain pollution
64 sources: for example, it was found that the prevalence of lower molecular weight PAHs in
65 ambient air samples can be essentially related to the road traffic, more specifically with vehicles
66 of diesel engines (Albuquerque et al. 2016). Studies on some specific PAH content ratios in
67 needles, such as anthracene/(anthracene + phenanthrene) or fluoranthene/(fluoranthene +

68 pyrene), have been carried out to identify local sources of contamination (Esen et al. 2008;
69 Galarneau 2008; Kong et al. 2015).

70 In this study, *Abies holophylla* needles from 1 to 6 years old (2016 – 2011) and *Pinus*
71 *tabuliformis* from 1 to 4 years old (2015 – 2012) have been collected to investigate the species–
72 specificity historical variations of PAHs and to examine the possible relation between emitted
73 air pollutants and PAHs in the needles over the years. To pursue this target, PAH degradation
74 has been taken into consideration using a first-order kinetic mechanism already used to interpret
75 the PAH degradation process (Wammer and Peters 2005). Finally, through a statistical approach,
76 potential correlations between PAH contents in conifer needles and data relevant to pollutant
77 sources of airborne PAHs in Jilin Province have been investigated.

78 **2. Material and methods**

79 **2.1 Materials and standards**

80 Standard mixtures of 16 PAHs (naphthalene (Naph), acenaphthylene (Acy), acenaphthene
81 (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr),
82 benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF),
83 benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd] pyrene (IcdP),
84 dibenzo[a,h]anthracene (DahA) and benzo[ghi]perylene (BghiP)) and 3 deuterated PAHs
85 (Phenanthrene-d₈, Fluoranthene-d₁₂ and Perylene-d₁₂) were purchased from Sigma Aldrich (St.
86 Louis, MO, USA). The purity of all standards was up to 98%. Silica (100-200 mesh) and Al₂O₃
87 adsorbent were obtained from Sigma Aldrich (St. Louis, MO, USA). To remove the
88 contaminants, all adsorbents and glassware were heated at 400°C for 12 h.

89 **2.2 Sampling and processing**

90 The sampling site was located on the west side of the Changbai Mountains, in the southeast
91 of Jilin Province, China. A detailed map of the sampling sites is reported in the Supplementary
92 Information (**Online resource 1**). Three different trees of *Pinus tabuliformis* and *Abies*
93 *holophylla* were chosen as sampling representative plants. Then, from each of them, leaf

94 samples (collected in October 2015 and October 2016) were selected and subdivided in function
95 of their age (*vide infra*), obtaining six fractions for *Abies holophylla* and four fractions for *Pinus*
96 *tabuliformis*, respectively. This sampling plan led to a total of 30 needle samples (3 trees \times 4
97 different needle ages for *Pinus tabuliformis*, and 3 trees \times 6 different needle ages for *Abies*
98 *holophylla*). The age of needles was evaluated following the directives of Pérez–Harguindeguy
99 et al. (Pérez–Harguindeguy et al. 2013), counting the number of rings of a branch cut close to
100 the needle samples (**Fig. 1**). In order to ensure the best sampling representativeness, needles of
101 the same year, collected between the upper 1/3 and lower 1/3 of the tree species canopy, were
102 mixed into one sample, and successively cleaned, freeze-dried, and crushed by 200 mesh. The
103 choice of this sieving grid dimension has been chosen on the basis of preliminary experiments,
104 which demonstrated that higher mesh values lead to a large sample loss during the sieving
105 process, while lower mesh values allow larger tissue shreds to pass through the mesh, making
106 the extraction process less efficient. Finally, if not directly analyzed, samples were stored at –
107 20°C.



108
109 **Fig. 1** Photographs that show the branch information of A) *Abies holophylla*, and the growth ring
110 patterns of B) *Abies holophylla* and C) *Pinus tabuliformis*.

111 Eleven air pollutant emission variables with an expected environmental impact on the PAH

112 concentrations, namely: coal (Ton year⁻¹), crude oil (Ton year⁻¹), and electricity (MkWh year⁻¹)
113 consumption; number of civil vehicles and trucks (Unit year⁻¹); emission of industrial sulfur,
114 nitrogen oxide, industrial smoke (dust), and soot (Ton year⁻¹); urban living gaseous pollutant
115 emissions (Ton year⁻¹); generating capacity (KWh year⁻¹), were obtained for the relevant areas
116 from the databases of the Jilin Provincial Bureau of Statistic (Jilin Province Statistics Bureau
117 Data Management Center 2020).

118 **2.3 Measurement of lipid content**

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

122 **2.4 PAHs analysis**

123 2.4.1 Extraction of PAHs

124 Sample pre-treatment procedures were performed according to a method already described
125 in our previous publication, with slight modifications (Jin et al. 2020). In brief, a total of 0.5 g
126 homogenized, crushed, and sieved needle powder was spiked with internal standards, then
127 mixed with 10 mL of dichloromethane (DCM) and ultrasonically extracted 3 times per 15 min.
128 The combined extract was dried under a gentle stream of nitrogen, replaced with n-hexane, and
129 concentrated to 0.5 mL prior to SPE clean-up. The SPE column (down-top: 2.0 g Na₂SO₄, 1.5
130 g silica gel, 0.8 g Al₂O₃ deactivated with 2% ultrapure water, and 4.0 g Na₂SO₄) was
131 conditioned with n-hexane before sample loading. Then, the extract was eluted with 3 mL n-
132 hexane (discarded) followed by 9 mL n-hexane/DCM (50: 50, v/v). The last 6 mL of the eluted
133 solution were collected and concentrated under a gentle stream of nitrogen gas at room
134 temperature, and subsequently reconstituted with 100 μL of n-hexane. Then, gas purge
135 microsyringe extraction (GP-MSE) was used for further purification, as described in a previous
136 work (Yang et al. 2011), and the final volume was adjusted to 100 μL. Finally, 2 μL of the
137 purified extract was injected into the gas chromatograph-mass spectrometer (GC-MS) for the

138 relevant analysis. All the samples were extracted in duplicate.

139 2.4.2 GC–MS analysis

140 PAH analyses were carried out by a Shimadzu GC equipped with a DB–5MS fused silica
141 capillary column (30 m × 0.25 mm; thickness: 0.25 μm, Restek Corporation, Bellefonte, PA,
142 USA) connected with a QPMS 2010 MS detector. GC–MS instrumental conditions were as
143 follows: sample injection was carried out in splitless mode at 280°C, using He as a carrier gas
144 at a flow rate of 1 ml min⁻¹. GC–MS interface temperature was set at 280°C, ionization voltage
145 was 70 eV, and ion source temperature was set at 200°C. The initial oven temperature was held
146 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
147 at 10°C min⁻¹ and 200°C to 280°C at 20°C min⁻¹, holding this last value for 2 min. Selected ion
148 monitoring mode (SIM) was selected for data collection.

149 2.5 Method validation

150 As recommended by the European Decision 657/2002/EC (European Community 2002),
151 the validation of the analytical methods is essential to provide reliable results in official controls
152 for pesticide determinations. Therefore, the analytical method was extensively validated
153 through the evaluation of selectivity, linearity, detection and quantification limits, precision,
154 recovery, and ruggedness. The absence of interfering peaks in the retention time window of
155 interest was checked for each analyte within the retention time tolerance of 0.2 min. The
156 trueness of measurements was assessed through the recovery of additions of known amounts of
157 the analytes to a blank matrix. Precision and recovery were determined by performing tests on
158 two sets of blank samples (n = 6), fortified with PAHs, each at a concentration of 200 ng mL⁻¹.
159 Spiked PAH samples at a concentration of 200 ng mL⁻¹ (n = 6) were analyzed for the validation
160 of the method in real samples. The experiments were carried out on different days with the same
161 instruments but by different operators, to ensure the greater variability of results. Limit of
162 detections (LODs) in leaf samples, calculated by 3 times the signal-to-noise ratios, were in the
163 range 0.02 – 0.08 ng g⁻¹. PAH method detection limits (MDLs), calculated as described by Jin

164 et al. (Jin et al. 2020), were in the range 0.2 – 5.1 ng g⁻¹. Under the optimized conditions,
165 recoveries obtained for standard solutions ranged from 79 to 99 %, while for matrix spiked
166 samples these values were from 64 to 120%. The relative percentage difference for individual
167 PAH determined in paired duplicate samples (n = 2) was always < 24%. The obtained recovery
168 for all the PAHs was between 64% and 120% with respect to the certified values.

169 **2.6 Statistical data treatment**

170 Precision and recovery data have been previously processed by the Shapiro-Wilk test
171 (Shapiro and Wilk 1965) to verify normal distribution. Afterward, a one-way ANOVA test was
172 performed to verify the homogeneity of the mean concentration values evaluated among the
173 validation sessions at each fortification level. The method reliability was assessed by the
174 analysis of blank samples (n = 6), standard solutions (n = 18), and spiked samples (n = 6). In
175 the case of blank samples, no significant response at 95 confidence level was observed for all
176 PAHs.

177 **3. Results and discussion**

178 **3.1 Adsorbed PAHs in needles**

179 Usually, the PAH content in plant samples is normalized by lipid content or dry weight.
180 Studies have shown that both cuticle and suberin (a cell wall component) may act as lipids in
181 different parts of the plant, but they are not solvent extractable (Ockenden et al. 1998; Taiz and
182 Zeiger 2010; Chen et al. 2012). For this reason, the needle lipid content obtained by these
183 methods may not reflect the total amount of PAH extracting substances. The needle lipid
184 contents in *Abies holophylla* and *Pinus tabuliformis* ranged from 27.46 to 32.16%, and from
185 6.85 to 9.56% (respect to dry weight), respectively (**Online Resource 2**). These values are
186 significantly different (at 95% confidence level) and undoubtedly influence the tendency of
187 different species to accumulate PAHs in the needles. In fact, *Abies holophylla* needles showed
188 a higher propensity to accumulate PAHs with respect to *Pinus tabuliformis* needles. On the
189 other hand, when a single tree species is considered, no significant correlation between lipid

190 content and PAH contents was found ($R = -0.12 - 0.646$, $p > 0.354$). Hence, in this study PAH
 191 contents were expressed on a dry weight basis. The sum of PAH contents found in leaf extracts
 192 (Σ PAHs) are listed in **Table 1**. As expected, due to the accumulating effect, Σ PAHs generally
 193 increase with the needle age, in accordance with the results obtained by previous works (Ratola
 194 et al. 2010a; Odabasi et al. 2015).

195 **Table 1** Σ PAHs (expressed on a dry weight basis) in *Abies holophylla* and *Pinus tabuliformis* as a
 196 function of needle age.

Rings	<i>Abies holophylla</i> (ng g ⁻¹) (n = 18)					
	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

197

Rings	<i>Pinus tabuliformis</i> (ng g ⁻¹) (n = 12)			
	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

198 3–4 ring PAH contents were found to be higher than 5–6 ring PAHs: this result is in good
 199 agreement with the PAH accumulation pattern in needles of other pine species, including *Pinus*
 200 *halepensis* and *Pinus pinea* (Librando et al. 2002), *Pinus pinaster* and *Pinus nigra* (Piccardo et
 201 al. 2005) and *Pinus pinaster* and *Pinus pinea* (Ratola et al. 2010a). The accumulation process
 202 may anyway vary from species to species, leading to a different concentration in needles (Ratola
 203 et al. 2011). This behavior has been noticed also for the species in this work, even if a similar
 204 PAH trend for years 1 to 4 with *Abies holophylla* and *Pinus tabuliformis* needles were noticed.
 205 More than 64% of adsorbed PAHs in the needles are composed of 3–4 ring PAHs: this value
 206 roughly reflects PAH composition in the air in both urban and industrial areas (Tomashuk et al.

207 2012; Odabasi et al. 2015; Li et al. 2016). The low content of 5–6 ring PAHs observed confirms
208 what already noticed in previous works (Albuquerque et al. 2016; Liu et al. 2017) and it is
209 prevalently due to their concentration in air, which is generally lower compared to the other
210 PAHs and by their different distribution in the environment. These PAHs are present, in fact,
211 preferentially in the particulate phase of the atmosphere, and for this reason, their migration
212 from the atmosphere can be slower if compared with other PAHs (Yang et al. 2017).
213 Furthermore, the low content of 5–6 ring PAHs could be also related to the fact that their
214 adsorption in needle leaves is more difficult due to their dimensions (Yang et al. 2007). 3–4 ring
215 PAHs, which are predominantly present in the gaseous phase, interact strongly with the waxy
216 layer of the needles and this effect can promote PAH uptakes in needles (Lehndorff and Schwark
217 2004). With regards to Naph, its volatile nature, its fast photodegradation process, and its re-
218 suspension capability lead to an unstable accumulation in the needles (Wang et al. 2005; Choi
219 2014).

220 3.2 PAH degradation constants in *Abies holophylla* needles

221 As already pointed out, PAHs are present in gas and particle phases of the atmosphere and
222 diffuse into plant leaves through dry and wet deposition. Their sources are closely related to the
223 anthropogenic combustion processes (e.g., car exhaust, local heating facilities, industrial-
224 related activities). It has been already demonstrated that the PAH degradation follows a first-
225 order kinetics (Wammer and Peters 2005; Haritash and Kaushik 2009), even if dependent on
226 external variables, like, for example, fly ash and carbon black, that can protect PAHs from
227 photodecomposition (Behymer and Hites, 1985; Korfmacher et al. 1979). Hence, it could be
228 hypothesised the PAH amount collected in different years by needles undergo a degradation
229 mechanism that follows an exponential trend. Considering, as a first approximation, that the
230 first-order degradation kinetic constant does not change over the years, the PAH total content
231 in leaves can be described by this equation:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

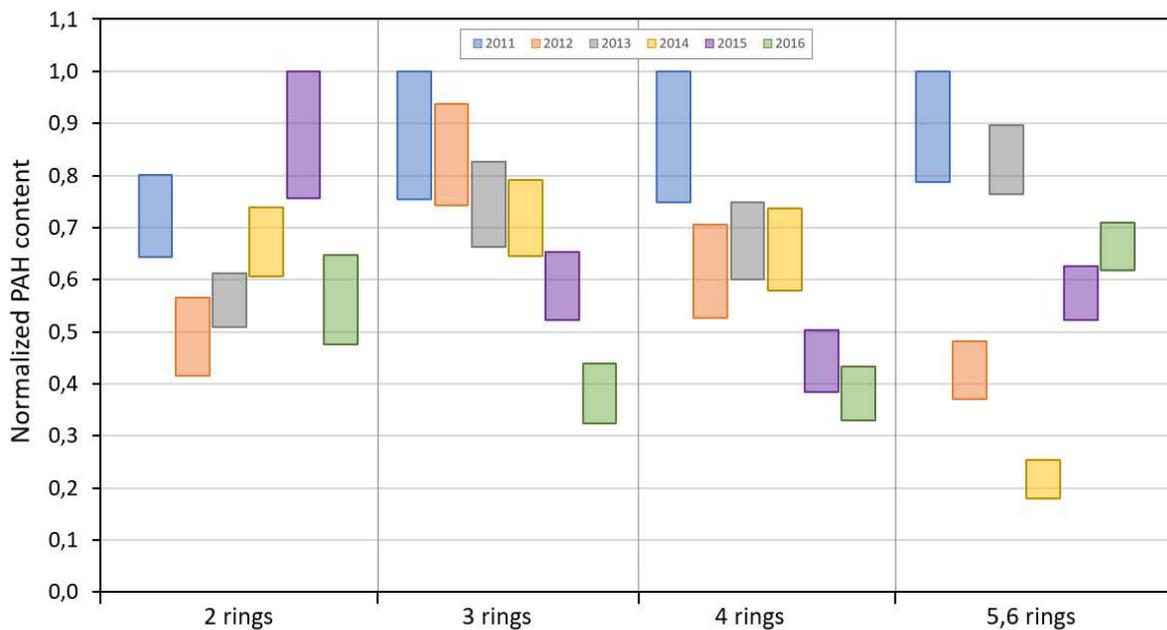
$$C_{2016}^{Tot} = C_{2015}^{Tot} y + C_{2016} \quad \text{Eq.13}$$

239 On the basis of **Eq. 9–13**, considering that C_{year} and y should be always ≥ 0 , it is possible
 240 to individuate the minimum acceptable α values and the relevant minimum PAH degradation
 241 percentage per year (**Table 2**) that satisfy this condition. Different works (Cutright 1995;
 242 Kästner et al. 1998; Johnsen et al. 2005) reported studies to determine the specific degradation
 243 rates for the bioremediation of PAH-contaminated soils, but, to our knowledge, no studies have
 244 been carried out regarding the PAH degradation in leaves.

245 **Table 2** Minimum percentage of PAH degradation year⁻¹ and minimum values of the degradation

Rings	Compound	Minimum degradation per year (%)	Minimum α 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

247 It is interesting to note that our results showed that the higher is the number of rings (i.e.
248 IcdP, DahA and BghiP), the higher is the degradation constant, while it has been demonstrated
249 that the degradation rate of high molecular weight PAHs in soil is slower than other PAHs
250 (Johnsen et al. 2005; Roslund et al. 2018). This different behavior is most probably ascribable
251 to the different degradation mechanisms in soil and needles: in the first case, it is governed by
252 bacteria activity, while in needles is mostly dependent on PAH chemical stability. The proposed
253 degradation model allows an estimation of the PAH contents retained by needles every year.
254 **Fig. 2** shows the normalized PAH content intervals in needles, with lower and upper limits
255 obtained considering the minimum α value listed in **Table 2** and the maximum PAH degradation
256 rates (i.e., $e^{-\alpha t} \simeq 0$), respectively. 3–4 ring PAHs show a decrease from 2011 to 2016, while for
257 2 and 5–6 ring PAHs the behavior seems not to follow any particular trend.



258

259 **Fig. 2** Normalized PAH content intervals in needles (calculated taking into account the PAH
 260 maximum concentration value for each ring class) through the years. Lower and upper limits
 261 have been obtained considering the minimum α value listed in Table 2 and the maximum PAH
 262 degradation rates (*i.e.*, $e^{-\alpha t} \approx 0$), respectively.

263 **3.3 Correlations between adsorbed PAHs in *Abies holophylla* needles and air pollutant**
 264 **emission variables in needles**

265 PAH sources are closely related to the anthropogenic combustion processes (e.g., car
 266 exhaust, local heating facilities, industrial-related activities). It has been already demonstrated
 267 that the presence of PAHs in Jilin Province area is mainly due to long-distance transportation
 268 and anthropogenic emission (Zhao et al. 2015). Then, it could be hypothesized a correlation
 269 between adsorbed PAHs and some air pollutant emission parameters, even if clearly influenced
 270 by the main wind in the sampling site, which is west-northwest in the spring, autumn, and
 271 winter, and southeast-southwest during the summer. From Jilin Provincial Bureau of Statistic
 272 (Jilin Province Statistics Bureau Data Management Center 2020), it has been possible to obtain
 273 data on the sampling areas concerning annual consumption of coal (Ton year⁻¹), crude oil (Ton
 274 year⁻¹) and electricity (MKh year⁻¹) consumption; number of civil vehicles and trucks (Unit
 275 year⁻¹); emission of industrial sulfur, nitrogen oxide, industrial smoke (dust), and soot (Ton

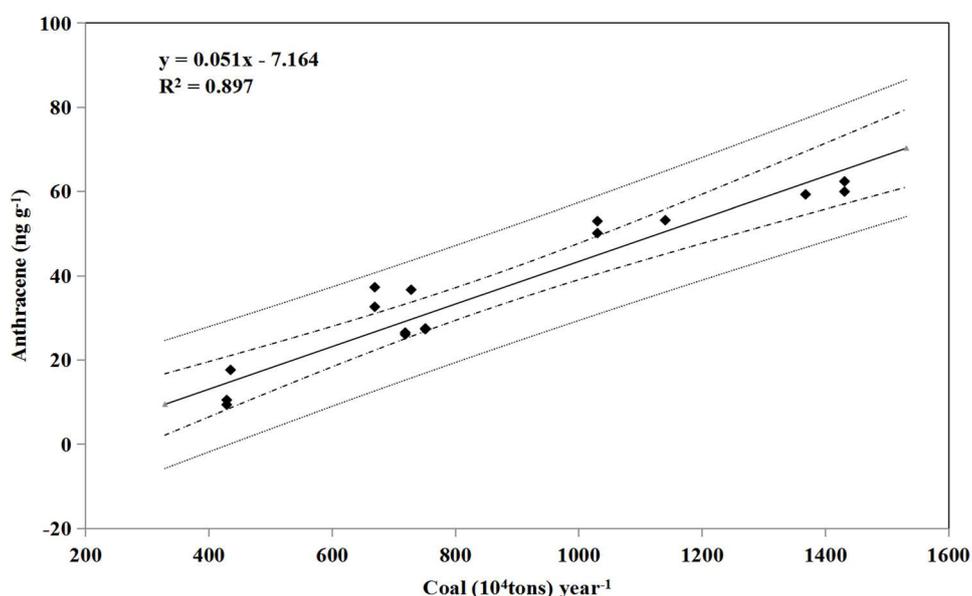
276 year⁻¹); urban living gaseous pollutant emissions (Ton year⁻¹); generating capacity (KWh year⁻
 277 ¹) (**Online resource 3**). Correlation coefficients were then obtained by linear regression
 278 considering these parameters and PAH average values from *Abies holophylla*. These values are
 279 reported in **Table 3**, where the most statistically significant correlations have been reported (R >
 280 0.8).

281 **Table 3** Correlation coefficients (R) obtained by linear regression between air pollution parameters and
 282 the average values of adsorbed PAHs obtained from *Abies holophylla*. Only R > 0.8 values are
 283 displayed. All these parameters are statistically significant ($\alpha = 0,01$, n = 18).

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

284 Some interesting considerations can be made based on **Table 3**. For instance, Phen, Fluo,
 285 and Ant (with correlation coefficients equal to 0.947, 0.915, and 0.874, respectively) are well

286 correlated with coal consumption, and this correlation can be ascribed to their large production
287 during this process (Dameng et al. 2011). On the other hand, these three PAHs are not the only
288 ones produced during coal combustion, but for these others, the lack of correlation could be due
289 to interfering processes. The correlation existing between the number of trucks and BbF can be
290 ascribed to its production by diesel engines (Kuusimäki et al. 2002). It is also worth to note the
291 high number of PAH that are correlated with industrial nitrogen oxide emissions, suggesting
292 that NO_x production can be strongly related to the emission of these PAHs in the atmosphere.
293 **Fig. 3** shows a typical correlation graph obtained between coal consumption per year and Ant
294 contents in needle.



295
296 **Fig. 3** Correlation between coal consumption per year and anthracene content in *Abies holophylla*
297 leaves. The solid line and dotted line curves represent confidence limits for the prediction and
298 confidence limits for the regression line at 95% confidence level, respectively.

299 In the urban areas, traffic emission is the dominant source of PAHs (Ratola et al. 2010b),
300 in particular for 3–4 ring PAHs: this could explain the significant correlation (at 95% confidence
301 level) between vehicle number and BaP. Surprisingly, none of the 5–6 ring PAHs shows
302 correlation with any of the pollution sources, probably because of their fast degradation constant
303 ($\alpha \geq 1.65$) that does not allow to acquire time dependent information from needles, and to the
304 molecule dimensions, that make more difficult their adsorption into pine needles (Yang et al.

305 2007).

306 **4. Conclusions**

307 In this study, the possibility to evaluate PAH historical changes and their correlation with
308 pollution emission sources by PAH contents in the needles of *Abies holophylla* and *Pinus*
309 *tabuliformis* has been investigated. Using the PAH content in *Abies holophylla* needles, a
310 mathematical model that considers a first-order PAH degradation process has been applied in
311 order to obtain the minimum α value for each of the considered PAH. Results indicate that the
312 higher is the number of rings (i.e. IcdP and DahA and BghiP), the higher is the degradation
313 constant in the needles, with the consequence of high degradation rates. Furthermore,
314 considering that PAH sources are closely related to the anthropogenic pollution processes, the
315 adsorbed PAH content calculated by the mathematical model used in this work from 2011 to
316 2016 in *Abies holophylla* leaves has been statistically compared with air pollutant emission
317 parameters achieved from the databases, obtaining in some cases correlation with $R > 0.8$
318 among data. The obtained results, which need further studies on a larger scale to confirm data
319 and correlations here presented, indicate that adsorbed PAHs in needle leaves are good
320 candidates as a biomonitoring system to evaluate the historical changes of PAHs induced by
321 pollutant emission on the regional scale.

322

323 **Author contributions** Z.W., M.H. and D.L. conceptualized and designed the experiments.
324 Z.W., X.J. and H.Y.K. performed the experiments. Z.W., M.Q. and J.L.Z. analyzed the data and
325 made figures. Z.W., Z.F. and M.Q. wrote the paper. All the authors read and contributed to the
326 submitted version of the manuscript. D.L. and M.H. acquired the funding and were responsible
327 for resources.

328 **Funding** This study was supported by a grant from the National Natural Science Foundation of
329 China (No. 21775134 & 22066025) and the 111 Project (D18012).

330 **Data Availability** All relevant data are within the manuscript and available from the

331 corresponding author upon request.

332 **Compliance with ethical standards**

333 **Conflict of interest:** The Authors declare that they have no conflict of interest

334 **Ethical approval:** Not applicable

335 **Consent to participate:** Not applicable

336 **Consent to publish:** Not applicable

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