Can *Abies alba* Needles Be Used as Bio-passive Samplers to Assess Air Quality?

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ABSTRACT

Bio-passive samplers have proved to be good alternate to assess air quality in regions where the use of active samplers is not technically feasible. Here, we tested the potential for *Abies alba* (silver fir) needles to be used as reliable bio-passive samplers. As these evergreen coniferous trees do not lose their needles in winter these are representative of a full year period. Needle samples were collected in 2013 from 20 different locations within the Holy Cross National Park (Świętokrzyski Park Narodowy, Holy Cross Voivodship, Poland). Both needles and the aerosols deposited on their surfaces were analyzed for their $\delta^{13}\text{C}$. Additionally, total carbon (TC), elemental carbon (EC) and organic carbon (OC) were determined only in surface-impacted aerosols using thermo-optical method. The overall objective of our study was to evaluate the possibility to distinguish bio-organic aerosols (crushed needles) from anthropogenically derived aerosols. The highest aerosol mass concentration ($4.6 \pm 2.4 \text{ mg g}^{-1}$) was observed in samples with the longest exposure time, while the shortest exposure times yielded the lowest ones ($1.7 \pm 0.7 \text{ mg g}^{-1}$). Aerosols that were enriched in ^{13}C , indicating the impact of human activities, were located close to inhabited areas, at highly elevated points and in places situated outside the park. Our results also prove that one-year-old needles are the most reliable isotope bioindicators. We ultimately recommend that *Abies alba* needles can be used in future air quality monitoring programs, especially since this method is low cost and easy to implement.

Keywords: Bioindicators, *Abies alba* needles, $\delta^{13}\text{C}$, Aerosols

1 INTRODUCTION

Atmospheric particulate matter (PM) is one of the major air pollutants in Europe (EEA, 2019) and carbonaceous aerosols represent one of the major PM components. This carbonaceous fraction is usually subdivided into organic carbon (OC), the light-scattering fraction, and elemental carbon (EC), the light-absorbing fraction (Galindo *et al.*, 2019; Xu *et al.*, 2015). Carbonate carbon (CC) bond to carbonaceous particles is less frequent (Ozdemir *et al.*, 2014). Organic carbon in atmospheric PM can originate from anthropogenic and natural sources and can be divided into two types: primary OC, emitted directly into the air and secondary OC, resulting from the secondary oxidation of VOCs by i.e., O_3 , NO_2 , OH (Murillo *et al.*, 2013; Kuchel *et al.*, 2016). Primary OC derives from natural biogenic sources (i.e., pollen, bacteria, viruses, several types of fungal spores, plants and fragments of insects) (Schwarz *et al.*, 2008). Secondary extractable OC, which includes VOCs from natural sources and anthropogenic compounds, should also be mentioned (Schauer *et al.*, 2007). Elemental carbon is a primary pollutant created directly from the incomplete combustion of fossil fuels or biomass (Galindo *et al.*, 2019). EC is characterized by a porous structure

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(Murillo *et al.*, 2013), which facilitates its adsorption of toxic compounds (Lucking *et al.*, 2011; Mills *et al.*, 2011). EC can be transported over thousands kilometers from its source, increasing its environmental impact (Husain *et al.*, 2007). Considering that, carbonaceous aerosols are of much interest when studying air quality. Another issue is analysis of carbon isotopes which can contribute to discrimination of the different sources of aerosols and has now been widely documented (e.g., Aguilera and Whigham, 2018; Górka *et al.*, 2012; Lim *et al.*, 2020; Morera-Gómez *et al.*, 2018; Widory *et al.*, 2004). These studies are based on the analysis of the different carbon isotope systematics: stable carbon isotopes ^{12}C , ^{13}C (e.g., Aguilera and Whigham, 2018; Morera-Gómez *et al.*, 2020) and/or radiocarbon ^{14}C (Lim *et al.*, 2020). Among the different sources, C_3 plants (in which the first product of the CO_2 assimilation during photosynthesis is a 3-phosphoglycerate – compound) are characterized by $\delta^{13}\text{C}$ from -34‰ to -24‰ (with an average of -27‰ (e.g., Šturm *et al.*, 2012; Zhang *et al.*, 2019). The major anthropogenic emission sources generate particles with the following typical $\delta^{13}\text{C}$ isotope compositions: (i) coal, between -24.2‰ (poor quality coal) and -25.7‰ (high quality coal), while the corresponding soot has a $\delta^{13}\text{C}$ of -24.5‰ (Górka and Jędrysek, 2008); (ii) diesel particles, from -26.5‰ (Widory *et al.*, 2004) to -28.3‰ (Górka and Jędrysek 2008); (iii) unleaded fuel particles, from -24.2‰ (Widory *et al.*, 2004) to -26.8‰ (Górka and Jędrysek, 2008).

It has now clearly been established that PM affects climate, the ecosystems and human health, especially in populated areas where it is present in significant concentrations (Atkinson *et al.*, 2015). Usually, such areas are under continuous control of the influence of anthropogenic sources. However, the rural sites can be also under serious risk in terms of air pollution but, unlike urban or industrial areas, they are usually not monitored. European Union requires that its member countries monitor their PM_{10} and $\text{PM}_{2.5}$ emissions as well as their ambient air concentrations (EEA *et al.*, 2018). In order to reach these objectives, active methods, which are based on a dynamic sampling and that require the use of a pumping device by which air passes through either an air sample container or a filter, are generally recommended. These methods are relatively expensive and require specific instrumentation. Hence, in some regions (e.g., mountain or woody) the implementation of this active sampling is often impossible due to the lack of access to electricity, altitude or limited access. The difficulty can be alleviated by the use of living organisms or their products (bioindicators) that are present in the targeted study areas. The use of bioindicators to monitor/assess the quality of different environments offers other advantages such as the possibility of bio-concentrating both organic and inorganic contaminants and of accessing time-integrated information (Conti and Cecchetti, 2001). Similarly to aerosol samples, bioindicators will yield information about the origin of the atmospheric particulate matter, from which the corresponding anthropogenic impact can be evaluated for a given area and time period. Bioindicators have already been proven to be excellent environmental proxies, from which pertinent information can be obtained by studying their carbon isotope compositions (e.g., Brendel *et al.*, 2003; Ciężka *et al.*, 2016). There are many kinds of different bioindicators, for example: lichens (e.g., Kłos *et al.*, 2007; Ciężka *et al.*, 2018; Kłos *et al.*, 2018), mosses (e.g., Kłos *et al.*, 2018; Maxhuni *et al.*, 2016; Shetekauri *et al.*, 2018), spider webs (Bartz *et al.*, 2021; Górka *et al.*, 2018; Stojanowska *et al.*, 2020; Stojanowska *et al.*, 2021). Also tree leaves and needles are considered useful bioindicator (Górka *et al.*, 2020; Lehnndorff and Schwark, 2004; Wang *et al.*, 2015; Wuytack *et al.*, 2010) as they have the capacity to accumulate particulate matter on their surface, that is further trapped by being covered with epicuticular wax (Zeisler-Diehl *et al.*, 2018). Tree needles are recording information about their surrounding air quality, such as potentially toxic elements or, indirectly, the carbon isotope compositions of depositing aerosols (e.g., Sensuła *et al.*, 2018; Vladimirovna Afanasyeva and Ayushievna Ayushina, 2019). The fact that the vegetation is highly spatially and temporally distributed makes it easily accessible and inexpensive in biomonitoring approaches (Sawidis *et al.*, 2011). Conifers are generally considered good bio-passive samplers as many of them are evergreen trees, i.e., they do not lose their needles in winter (Mauri *et al.*, 2016). Consequently, monitoring air quality using their needles can be carried out on a full year scale. The needles' adsorption potential is enhanced by the morphology of the conifers canopies, as they are dense and fine-textured with a high leaf area index (Yang *et al.*, 2015). To our knowledge, no study has ever been conducted on carbonaceous aerosols collected on needles, and in particular focusing on their carbon geochemistry and isotope compositions. With that in mind, our objective was to evaluate the possibility of using *Abies alba* needles as alternate

bioindicators to study air quality, using an approach that coupled the $\delta^{13}\text{C}$ from the needles and the aerosols adsorbed onto their surface with the total carbon (TC), elemental carbon (EC) and organic carbon (OC) contents of the aerosols.

2 MATERIALS AND METHODS

2.1 Study Area

Samples were collected in the Holy Cross National Park, located in the Holy Cross Voivodship, central Poland (Fig. 1). Several major emission sources are located in the vicinity of the study area (Fig. 1): power stations in Kielce, Połaniec, Jaworzno and Bełchatów; a steel plant in Ostrowiec; sulphur chemical plants in Grzybów and Tarnobrzeg; and a zinc smelter in Miasteczko Śląskie. Road traffic is another major local source of aerosols with an average of 8,500 cars/day driving the national roads of the Holy Cross Voivodship (GDDKiA, 2015). Heating in the Voivodship's single and multi-family buildings is mostly based on the combustion of poor-quality coal. The air quality in this region is also influenced by transboundary pollutant transport, mostly from the Lesser Poland and Silesian Voivodships, with carbon monoxide, nitrogen oxides and non-methane volatile organic compounds (NMVOC) representing the main transported compounds (Environmental protection program for the Holy Cross Province. Available at: <https://bip.sejmik.kielce.pl/142-departament-rozwoju-obszarow-wiejskich-i-srodowiska/4769-program-ochrony-srodowiska-dla-wojewodztwa-swietokrzyskiego-na-lata-2015-2020-z-uwzglednieniem-perspektywy-do-roku-2025.html>; accessed September 16, 2019).

2.2 Materials

Abies alba (silver fir) was selected as it represents the most abundant tree in the Holy Cross National Park and its needles are easily accessible. All needle samples were collected in summer 2013 at 20 different locations: 18 in the National Park and 2 in its close vicinity (Fig. 1). At each sampling location, branches from a few trees (typically 5) were collected at a height about 1.5–2 meters above the ground and pooled to both homogenize the needle samples and obtain a sufficient amount of material for the subsequent analysis (generally 15 g). The needles were packed in clean paper bags for transport. To avoid any potential canopy effect between the sampled trees, they were chosen within similar populations. In the laboratory, needles were divided by age classes (6-months old, referred as 2013; 1-year-old, referred as 2012; and older than 1 year, referred as < 2012), weighed and stored in paper bags: 3 samples were thus obtained for each sampling location, for a total of 60 samples. The age division was made taking into consideration the needle growth on branches and the noticeable separation of their individual annual increments. This also allowed to obtain samples with different aerosol collection times that later will permit testing the needle potential and efficiency for collecting aerosols. This protocol for separating needles was adapted from Brendel *et al.* (2003) and Muukkonen and Lehtonen (2004).

2.3 Methods

2.3.1 Samples preparation

Aerosols were washed out of the needles' surface using distilled water as previous studies demonstrated that this washing agent gives satisfying results (e.g., Al-Alawi and Mandiwana, 2007; Ataabadi *et al.*, 2011; Leśniewicz and Zyrnicki, 2000). In brief, ~15 g of needles were placed into a beaker. 300 mL of distilled water were added and the beaker was gently mixed with a glass rod for 5 minutes. This five-minute mixing was determined by trial and error: longer than 5' caused a large number of needles to crumble, while a shorter time resulted in a low aerosol yield. The solution was then filtered through a QM-A quartz fiber filter (diameter of 47 mm, porosity 2.2 μm , Whatman) under vacuum. Quartz fiber filters were not baked before collection according to the fact that previous studies from our research group demonstrated that blank filters yielded carbon contents under the CM-CRDS detection limit. After filtration filters were dried in an oven at $45 \pm 2^\circ\text{C}$ and stored in a desiccator until further treatment and analysis. The filters were double weighed before and after the filtration using a Vibra HTR-220CE (± 0.1 mg, at $23 \pm 2^\circ\text{C}$ and relative humidity of $40 \pm 5\%$), yielding the mass of particulate matter adsorbed on the needles. The final PM quantity was expressed as milligrams of aerosols per gram of dry needles.

2.3.2 Carbon stable isotope analysis ($\delta^{13}\text{C}$) of aerosol and needle samples

$\delta^{13}\text{C}$ isotope compositions were determined by Cavity Ring-Down Spectroscopy (CRDS) coupled to a combustion module. For filter samples, a punch was cut using an IVA Analysentechnik puncher. Needle samples were homogenized by grounding them in a clean fine grit mill. Both the size of the punch and the mass of grounded needles were adjusted during each run to ultimately obtain ~2000–4000 ppm of CO_2 generated by the combustion process. For the carbon stable isotope analysis, the filter punch or the needle powder was placed into a tin capsule that was sealed and analyzed using a Picarro G2201-i CRDS analyzer coupled with a CM (combustion module). Carbon isotope compositions were expressed as $\delta^{13}\text{C}$ values, which represent the relative difference expressed in per mil (‰) between the isotope ratio of the sample and that of the Pee Dee Belemnite (PDB) standard:

$$\delta^{13}\text{C} (\text{‰ vs. PDB}) = R_{\text{sample}}/R_{\text{PDB}} - 1 \times 1000 \quad (1)$$

$\delta^{13}\text{C}$ values were calibrated using certified standards NBS-19 ($\delta^{13}\text{C} = +1.95\text{‰}$), NBS-18 ($\delta^{13}\text{C} = -5.014\text{‰}$), IAEA CO-8 ($\delta^{13}\text{C} = -5.764\text{‰}$), USGS-24 ($\delta^{13}\text{C} = -16.049\text{‰}$) and USGS-40 ($\delta^{13}\text{C} = -26.389\text{‰}$). Analyses were made on 2 to 4 replicates and the associated analytical error on the measured $\delta^{13}\text{C}$ was $< 0.2\text{‰}$.

2.3.3 Total carbon, organic carbon and elemental carbon quantification in aerosols

Total carbon (TC), elemental carbon (EC) and organic carbon (OC) were determined using a Sunset Laboratory Dual-Optical Carbonaceous Analyzer at the University of Gdansk (Division of Marine Chemistry and Environmental Protection, Institute of Oceanography). We followed the EUSAAR2 protocol, owing to the optimal maximum temperature obtained at the end of the first stage, which corresponded to 650°C , and ensured that only $2.5 \pm 2.4\%$ of the elemental carbon was combusted during the first stage of analysis (Cavalli *et al.*, 2010). A 1.5 cm^2 rectangular piece of the quartz fiber filter was placed into a quartz oven, where it was analyzed for both OC and EC. The method's limit of detection (MLD) was $0.3 \mu\text{g cm}^{-2}$ ($n = 72$) for both OC and EC, while the analytical error was $< 6\%$ for EC and $< 10\%$ for OC (with a 99% confidence interval). All carbon results were corrected for blanks: $3.0 \mu\text{g cm}^{-2}$ for OC while no correction was necessary for EC as blanks were under the MLD. Apart from automatic calibration (internal standard: 5.0% methane in equilibrium with analytically pure He), which takes place at the end of the second stage of the analysis, an external standard was analyzed (99% analytically pure sugar solution) after every 10–15 samples. The average analytical error of the external calibration was 4.5%. Additionally, an inter-laboratory comparison using an Elemental Analyzer Instruments NC 2500 NC at the Université du Québec à Montréal (UQAM) was performed. The agreement between the two methods was confirmed by a high Pearson correlation coefficient value for total carbon ($r > 0.9$). More details can be found in our previous publications (Lewandowska *et al.*, 2018; Wiśniewska *et al.*, 2019).

2.3.4 Isotope mass balance calculation

We performed an Isotope Mass Balance (IMB) to estimate the respective contributions of the following 2 endmembers on the final $\delta^{13}\text{C}_{\text{aerosols}}$ we measured: contamination (i.e., external) and biogenic (i.e., needle). Contributions were calculated using the following equation:

$$\text{IMB} = a \times \delta^{13}\text{C}_{\text{source}} + b \times \delta^{13}\text{C}_{\text{needles}} = \delta^{13}\text{C}_{\text{aerosols}} \quad (2)$$

where $\delta^{13}\text{C}_{\text{aerosols}}$, $\delta^{13}\text{C}_{\text{needles}}$ and $\delta^{13}\text{C}_{\text{source}}$ are the $\delta^{13}\text{C}$ of the aerosols, needles and of the corresponding aerosol emission source. “a” is the percentage contribution of the contaminant source and “b” the one of particles resulting from the eventual inclusion of needle debris during the sample preparation, when needles are washed with distilled water.

2.3.5 Statistical analysis

We used the Kruskal-Wallis test to highlight differences between dust concentrations with respect to the different needle age classes. To discriminate groups, multiple pairwise-comparisons

using the Dunn's test were applied. These median tests are the non-parametric equivalent of ANOVA and allow to evaluate differences between more than 2 variables. Tests were performed on the 60 samples using the computing environment R (R Core Team, 2013; additional software packages tidyverse, ggpubr, rstatix and ggplot2 were used). Multivariate Principal Component Analysis (PCA) was performed on 5 standardized parameters measured in dust (for 2012 needles): dust concentration, TC, EC, OC and $\delta^{13}\text{C}$. The objective of the PCA (Statistica 13 software) was to identify the interrelated factors characterizing the processes controlling the dust carbon chemical and isotope compositions. Transformation factor loads matrix (varimax rotation; Table 3) and factor scores values (Fig. 9) were calculated (Cattell, 1966; Drever, 1997; Johnson, 1978). As it was demonstrated by Manly (1998) PCA requires a limited number of useful variables and it helps to describe relations amongst them. The PCA results were considered reliable due to the high number of samples (58) analysed, the observed normal distribution (for $\delta^{13}\text{C}$) or close to normal or lognormal for the other data, and the correct conditioning of the matrix as well as eigenvalues close to 1 for the parameters. The Surfer 10.0 software was used to create the isoline maps (Figs. 3, 5, and 7), applying an ordinary kriging method.

2.3.6 Scanning electron microscope (SEM) analysis

SEM analysis, on a randomly-selected subset of samples, was conducted in order to investigate i) if the our protocol (i.e., rinsing with distilled water) was efficient at washing out the aerosols deposited at the surface of the needle samples and ii) to verify that the surface of the needles had not been damaged by the subsequent stirring, which may have impacted the $\delta^{13}\text{C}$ analysis. Fig. 2 reports the SEM images of the adaxial surface of the several-years-old samples (< 2012),

Fig. 2. SEM images (A) before and (B) after washing out with distilled water. The needle sample shown here corresponds to the age class < 2012 .

Table 1. Statistics on needle samples from the different age classes.

< 2012														2012							2013						
Aerosols concentration [mg g ⁻¹]														Aerosols concentration [mg g ⁻¹]							Aerosols concentration [mg g ⁻¹]						
C [%]														C [%]							C [%]						
TC [mg g ⁻¹]														TC [mg g ⁻¹]							TC [mg g ⁻¹]						
EC [mg g ⁻¹]														EC [mg g ⁻¹]							EC [mg g ⁻¹]						
OC [mg g ⁻¹]														OC [mg g ⁻¹]							OC [mg g ⁻¹]						
$\delta^{13}\text{C}_{\text{aerosols}}$														$\delta^{13}\text{C}_{\text{aerosols}}$							$\delta^{13}\text{C}_{\text{aerosols}}$						
$\delta^{13}\text{C}_{\text{needle}}$														$\delta^{13}\text{C}_{\text{needle}}$							$\delta^{13}\text{C}_{\text{needle}}$						
Average	4.6	35	1.48	0.05	1.43	-29.5	-32.1	3.2	41	1.28	0.06	1.23	-29.3	-32.1	1.7	46	0.72	0.03	0.70	-29.7	-31.9						
Median	4.4	35	1.46	0.04	1.44	-29.3	-32.0	2.8	41	1.12	0.05	1.01	-29.3	-32.2	1.8	41	0.77	0.02	0.75	-29.7	-32.1						
SD	2.4	7	0.64	0.04	0.62	1.0	1.3	1.2	9	0.53	0.02	0.54	1.1	1.3	0.7	16	0.18	0.01	0.17	1.0	1.3						
Maximum	11.3	53	2.68	0.18	2.65	-28.2	-29.4	5.5	54	2.37	0.11	2.32	-27.2	-29.4	3.2	97	1.01	0.06	0.94	-27.6	-29.7						
Minimum	2.0	26	0.65	0.01	0.61	-31.3	-34.4	1.8	11	0.58	0.02	0.47	-31.2	-34.5	0.3	25	0.33	0.01	0.33	-31.3	-34.1						

before (Fig. 2(A)) and after washing (Fig. 2(B)). The comparison between the two images confirms that aerosols were successfully washed out without damaging the surface of the needles although we acknowledge that some small quantities of needle fragments may still have been collected concomitantly with the aerosols.

3 RESULTS

3.1 Aerosol Concentrations and TC, OC and EC Values

Concentrations of aerosols adsorbed on the needle samples are reported in Table 1. The highest concentrations were on average 4.6 ± 2.4 mg g⁻¹ and corresponded to the oldest samples (< 2012; > 1 year). In contrast, the lowest concentrations (average of 1.7 ± 0.7 mg g⁻¹) corresponded to samples collected in 2013, the shortest exposure time of our study (< 1 year). The aerosol concentrations measured for the year 2012 ranged from 1.8 to 5.5 mg g⁻¹, with an intermediate average value of 3.2 ± 1.2 mg g⁻¹.

In the case of TC, EC, and OC the results also varied depending on the age of the samples. The average TC results were as follows: 1.48 ± 0.64 mg g⁻¹, 1.28 ± 0.53 mg g⁻¹, 0.72 ± 0.18 mg g⁻¹ for < 2012, 2012, and 2013 respectively. The respective OC averages of 1.43 ± 0.62 mg g⁻¹ for samples older than 2012, 1.23 ± 0.54 mg g⁻¹ for 2012 and 0.70 ± 0.17 mg g⁻¹ for 2013 were noted (Table 1). The concentrations of EC were very low, revealing 0.05 ± 0.04 , 0.06 ± 0.02 and 0.03 ± 0.01 mg g⁻¹ for < 2012, 2012, and 2013 respectively.

3.2 Aerosol and Needle Carbon Isotope Compositions

The samples marked as older than 2012 were characterized by $\delta^{13}\text{C}_{\text{aerosols}}$ equal to $-29.5 \pm 1\text{‰}$ and $\delta^{13}\text{C}_{\text{needle}}$ equal to $-32.1 \pm 1.3\text{‰}$. On the other hand, one-year old samples (2012) revealed averages of $\delta^{13}\text{C}_{\text{aerosols}}$ and $\delta^{13}\text{C}_{\text{needle}}$ equal to $-29.3 \pm 1.1\text{‰}$ and $-32.1 \pm 1.3\text{‰}$, respectively. The samples with the shortest exposure time yielded $\delta^{13}\text{C}_{\text{aerosols}}$ equal to $-29.7 \pm 1\text{‰}$ and $\delta^{13}\text{C}_{\text{needle}}$ equal to $-31.9 \pm 1.3\text{‰}$ (Table 1).

4 DISCUSSION

4.1 Concentrations of Adsorbed Aerosols

It seems that results of concentrations of adsorbed aerosols are correlated to their age, i.e., exposure time to ambient air, with the shorter exposure times yielding lower PM concentrations (Table 1). The increasing trend observed for the aerosol concentrations on the surface of the needles confirm that they can be used as passive samplers for characterizing air quality. Previous studies have shown that plants in general play a significant role in removing atmospheric particulate matter (e.g., Nowak *et al.*, 2013) due to their capacity to accumulate PM, which depends on the properties of the leaf surfaces (Wang *et al.*, 2015). Leaf and needle surfaces consist of cuticles and an epicuticular wax, the outer surface of the cuticle (Buschhaus and Jetter, 2011; Zeisler-Diehl *et al.*, 2018) that protect plants from water loss, UV light and abiotic stress factors (Zeisler-Diehl *et al.*, 2018). The structure of the needle surface facilitates the adsorption of aerosols and once deposited they are not easily removed by wind or rainfall. Moreover, aerosols, deposited on the needle surface can block the substomatal chambers (Teper, 2009). This may lead to i) a decrease in the photosynthesis rate by reducing sunlight availability, ii) an increase in the leaf temperature triggered by changes in the surface optical properties, and iii) a modification of gas diffusion into and out of the leaves (Prajapati and Tripathi, 2008; Squires, 2016).

As a result, the basic functions of the plant are disrupted and the damaged fragments become susceptible to fungal infections (Teper, 2009). If needle samples are covered by fungi this may ultimately limit their potential to adsorb aerosols.

Additionally, the concentrations of adsorbed aerosols in our study area varied greatly, seemingly depending on the proximity to anthropogenic sources (Fig. 3). Cieżka *et al.* (2018) previously studied air quality in the Holy Cross National Park using passive samplers (NO₂ and SO₂ concentrations) and bioindicators (heavy metals in *Hypogymnia physodes*). The authors concluded that air quality in our study area is impacted by emissions from local and regional anthropogenic sources (fossil fuel combustion; Cieżka *et al.*, 2018): i) the impact of gaseous pollutants increased during heating season; ii) higher NO₂ concentrations were observed along roads; iii) higher SO₂ concentrations were observed at higher elevations; and iv) the highest Zn, Pb and Cu concentrations in bioindicators were recorded at high altitude and were linked to long-range transport. Our results are showing similar trends, independently of the age of the needles (Fig. 3). Still, Fig. 3 shows that aerosol concentrations were higher in the older needle samples and seem positively related to their age (i.e., exposure time).

The lowest aerosol concentrations were observed in 6-months old samples (2013; Fig. 3(A)). The samples were collected during the summer 2013, implying that in these 6-months old samples the corresponding adsorbed aerosols were mainly emitted by natural sources or/and resulted of long-range transport, but were not linked to emissions from home-heating. The one-year-old samples (2012) revealed the highest aerosol concentrations at sampling locations 4, 12 and 13 (Fig. 3(B)). These same sampling locations were also characterized by the highest aerosol concentrations for samples with the longest exposure time (Fig. 3(C)). This may result from transboundary transport: sampling location 12 is the highest elevation while sampling location 4 is located in the close vicinity of an inhabited area. Pairwise comparisons using the Dunn's test showed that among the needle groups, the < 2012 and 2013 group and the 2012 and 2013 groups were significantly different (Fig. 4).

4.2 Aerosol and Needle Carbon Isotope Compositions

Our results show that aerosols adsorbed on the needles were enriched in ¹³C (i.e., higher $\delta^{13}\text{C}$), especially for samples collected close to inhabited areas (3, 4, 6), at the station located outside the park (20) as well as at the high-elevation ones (11, 12 and 15) (Fig. 5). For this latest group of samples, the increase in the $\delta^{13}\text{C}$ may be associated to transboundary contamination. South-western winds dominate in the study area (Olszewski *et al.*, 2000) and bring air pollutants from other Voivodships (especially from the Lesser Poland and the Silesian ones). This hypothesis is comforted by the fact that the highest $\delta^{13}\text{C}$ we measured corresponded to locations in the southern part of the park (around sampling location 15 and further south; Fig. 5).

Variations of the $\delta^{13}\text{C}_{\text{needle}}$ were as follows: i) for the oldest samples (< 2012) carbon isotope

Fig. 3. Concentrations of aerosols deposited on needle samples. (A) 2013 samples, (B) 2012 samples, (C) < 2012 samples.

compositions varied between -34.4 and -29.4% , ii) 2012 samples varied between -34.5 and -29.4% and iii) those of 2013 between -34.1 and -29.7% . However, while we observed small variations in the average $\delta^{13}\text{C}_{\text{needle}}$ values (around $\pm 0.2\%$, i.e., similar to the analytical error),

Fig. 4. Distribution of the aerosol concentrations as a function of the needle age.

differencing the different sampling years was not possible. In fact, the $\delta^{13}\text{C}_{\text{needle}}$ variations seemed more correlated to the sampling location than to exposition duration. Isotope variations generally result from numerous factors. One of them could be the Suess effect, which corresponds to a change in both the ^{13}C and ^{14}C ratios following the emissions of large amounts of fossil-fuel derived CO_2 , although its influence is not fully understood (Sensuła *et al.*, 2018). The $\delta^{13}\text{C}$ difference between needles of different ages from the same sampling locations did not exceed 1‰ (SM Table 1). This may be explained by the fact that even if the time of sampling was the same (summer 2013) for all needle samples, the duration of their exposure to air pollution was different. Consequently, it was difficult to compare our results with previous similar studies, especially with that of Sensuła *et al.* (2018) who studied yearly collected needles (i.e., no variation in the duration of exposure to air pollution). Precipitations and humidity are two other important factors that control the $\delta^{13}\text{C}$ of plants. Cuna *et al.* (2007) suggested that a higher amount of precipitations leads to a ^{13}C -depletion (i.e., lower $\delta^{13}\text{C}$) of the plant $\delta^{13}\text{C}_{\text{org}}$. This comes from the fact that under humid conditions ^{12}C -enriched components are preferably accumulated, inducing a negative correlation between the $\delta^{13}\text{C}$ of the plant and the prevailing relative humidity (Cuna *et al.*, 2007). Air humidity and soil moisture also control the $\delta^{13}\text{C}$ values of tree rings (e.g., Gagen *et al.*, 2007; McCarroll and Pawellek, 2001; Pazdur *et al.*, 2013). Cuna *et al.* (2007) showed that elevation also impact carbon isotope compositions, showing that lichens collected at high elevations were enriched in ^{13}C , and linked it to the increase in the atmospheric ozone concentrations with altitude: the excess of ozone induces a decrease in photosynthesis, leading to a ^{13}C -enrichment. Ozone levels in Poland may vary depending on the time of year (GIOŚ, 2019). Finally, the canopy effect can also impact the $\delta^{13}\text{C}_{\text{needle}}$, with the most negative values supposed to be measured close to the ground surface (Merwe and Medina, 1991). However, here, in order to cancel the canopy effect within each sampling location, we selected and sampled trees growing in groups within a similar population. To summarize, many distinct factors can influence the carbon isotope compositions of needles, making the interpretation of the $\delta^{13}\text{C}_{\text{needle}}$ values difficult. Here, while we did not observe a significant time-related isotope discrimination, the location of collection seems nevertheless to influence the measured $\delta^{13}\text{C}_{\text{needle}}$.

Fig. 5. Carbon isotope compositions ($\delta^{13}\text{C}$) of the deposited aerosols. (A) 2013 samples, (B) 2012 samples, (C) < 2012 samples.

As discussed, the analysis of the $\delta^{13}\text{C}$ of needles and aerosols may bring critical information about the corresponding contamination sources. But we first had to assure that the collected aerosol samples were not largely contaminated by crushed needles during the preparation protocol, which would artificially shift the $\delta^{13}\text{C}$ value we are attributing to the aerosols. We hypothesized that $\delta^{13}\text{C}$ of the deposited aerosols is different from that of needles. Additionally, we postulated that

higher differences between $\delta^{13}\text{C}_{\text{aerosols}}$ and $\delta^{13}\text{C}_{\text{needle}}$ indicate a higher contribution of anthropogenic aerosols. Finally, we used a Isotope Mass Balance to estimate the respective contributions of the different contributing emission sources (Table 2).

As our old samples (< 2012) were covered by high amount of organic particles and those of 2013 represented only the vegetative season, the IMB was only run for the 2012 needles and their aerosols, as they were exposed to air contamination during both vegetative and heating season. We also ran the IMB considering two distinct scenarios for the source of air contamination: i) the emission source is local and mostly correspond to road traffic in the park. Its carbon isotope composition was calculated considering the respective particle contributions of typical Wrocław road traffic (Central Statistical Office, 2013) and $\delta^{13}\text{C}$ (–28.3‰ for diesel and –26.8‰ for unleaded; Górka and Jędrysek 2008: $\delta^{13}\text{C}_{\text{source}} = 2/3 \delta^{13}\text{C}_{\text{diesel}} + 1/3 \delta^{13}\text{C}_{\text{unleaded}} = -27.8\text{‰}$), ii) the emission source corresponds to home heating with a $\delta^{13}\text{C}$ of –24.5‰ (Górka and Jędrysek, 2008).

Previous studies have shown that using bioindicators in environmental monitoring impacts the size of the aerosols collected. Teper (2009) demonstrated that for pine needles most of the particles collected are < 10 μm as larger ones are possibly washed out by rain. On the other hand, Freyer (1978) showed that, as deposition velocity is higher for fine or ultra-fine particles, conifers preferentially collect the coarse fraction. Moreover, Bartz *et al.* (2021) concluded that the fine fraction presents higher physical and chemical heterogeneities as it is generally connected to anthropogenic emissions. Ultimately, we can hypothesize that the fraction of fine aerosols collected on our pine needles was less abundant, rendering the identification of their emission sources difficult.

Results (Table 2) indicated that if we consider that calculated contributions > 70% are significant, road traffic (referred as the a_1 value) had the strongest influence on sampling points located close to inhabited areas (3, 4, 6; Fig. 1), elevated areas (11, 15), at the sampling location outside the National Park (20) and at location 13. Also, for all samples the contribution of road traffic was dominant, the contribution of home heating being always secondary. Moreover, in scenario 2 the calculated a_2 values were almost always lower than the b_2 ones, which indicated a higher influence of particles from crushed needles. Sample 13, located in a residential area and very close to a busy road, identified significant contributions from both road traffic and home

Table 2. Isotope Mass Balance calculations, showing the respective contributions of the contaminant source and crushed needles in aerosol samples (i.e., one-year old samples (2012)).

Sampling point	$\delta^{13}\text{C}_{\text{aerosols}}$	$\delta^{13}\text{C}_{\text{needle}}$	$\Delta\delta^{13}\text{C}_{\text{aerosols}} - \delta^{13}\text{C}_{\text{needle}}$	Road traffic		Home heating	
				a_1	b_1	a_2	b_2
1	–29.7	–31.6	1.9	0.50	0.50	0.27	0.73
2	–31.1	–33.1	2.0	0.38	0.62	0.24	0.76
3*	–27.6	–29.4	1.8	1.16	–0.16	0.38	0.62
4	–28.1	–30.9	2.8	0.90	0.10	0.44	0.56
5	–31.2	–33.9	2.7	0.45	0.55	0.29	0.71
6	–28.5	–32.2	3.7	0.84	0.16	0.48	0.52
7	–29.4	–32.8	3.4	0.69	0.31	0.41	0.59
8	–29.5	–32.1	2.6	0.61	0.39	0.34	0.66
9	–30.2	–33.7	3.5	0.59	0.41	0.38	0.62
10	–29.0	–31.8	2.8	0.70	0.30	0.38	0.62
11	–28.9	–32.3	3.4	0.76	0.24	0.44	0.56
12	–28.9	–30.9	2.0	0.66	0.34	0.32	0.68
13	–28.9	–34.5	5.6	0.84	0.16	0.56	0.44
14	–29.3	–32.4	3.1	0.68	0.32	0.39	0.61
15	–27.9	–31.0	3.1	0.98	0.02	0.48	0.52
16	–29.6	–33.4	3.8	0.68	0.32	0.43	0.57
17	–29.6	–32.6	3.0	0.63	0.37	0.37	0.63
18	–30.9	–31.6	0.7	0.18	0.82	0.10	0.90
19	–29.8	–32.3	2.5	0.56	0.44	0.32	0.68
20	–28.3	–30.2	1.9	0.81	0.19	0.34	0.66

* In this sampling point the mixture of diesel and unleaded has different proportion than the one assumed by us.

heating, and was the only sampling location where these contributions (a_1 and a_2) were higher than those of crushed needles (b_1 and b_2).

Results also confirmed our hypothesis that the isotope difference (Δ) between the two isotope compositions ($\delta^{13}\text{C}_{\text{aerosol}} - \delta^{13}\text{C}_{\text{needle}}$) is a good proxy of the anthropogenic impact. In the Holy Cross National Park, the highest Δ values were observed at sampling locations 13, 16, 6 and 9 with carbon isotope fractionations of 5.6‰, 3.8‰, 3.7‰ and 3.5‰, respectively. Location 9 is in the immediate vicinity of a busy road. For sampling locations 6, 13 and 16 local home heating and road traffic were the most probable sources of contamination. To a lesser extent, lower but still significant Δ values were also observed at highly elevated sampling locations, which may indicate that their $\delta^{13}\text{C}$ was controlled by air masses transported from distant areas or higher ozone concentrations.

4.3 Relationships between $\delta^{13}\text{C}_{\text{aerosols}}$ and $\delta^{13}\text{C}_{\text{needle}}$

Fig. 6 reports the $\delta^{13}\text{C}$ variations of the total carbon between the needles and the deposited aerosols. Results show that deposited aerosols samples were all enriched in ^{13}C compared to the needles they were deposited on, which indicates that the collected aerosol particles were not dominated by needle-derived fragments.

Needle samples with several years of exposition were expected to yield the lowest $\delta^{13}\text{C}$ values as their longer exposure time and subsequent accumulation of aerosols are propitious to fungal growth, that will ultimately impact their carbon isotope compositions. Meanwhile, one-year-old needle samples (2012, i.e., that were exposed to air pollution during growing and heating

Fig. 6. Relationship existing between the $\delta^{13}\text{C}$ of needles and that of deposited aerosols.

seasons) were expected to record the highest $\delta^{13}\text{C}$ values resulting from the incorporation of ^{13}C -enriched aerosols from road traffic and home heating ($\delta^{13}\text{C} > -24.5\text{‰}$). Finally, 6-months-old needle samples (2013; i.e., that were not exposed to emissions from heating sources) were expected to present $\delta^{13}\text{C}$ values mostly corresponding to road traffic. Results from Fig. 6 show that only samples from location 3 follow this trend. Needle samples older than 2012 exhibited the greatest fungal growth, similar to the findings of Teper (2009), who suggested that this class of needles (i.e., older than one year) should not be used as isotope bioindicators due to their elevated amount of natural particles that ultimately modifies the final $\delta^{13}\text{C}$.

4.4 Total Carbon (TC), Organic Carbon (OC) and Elemental Carbon (EC) Concentrations

The analysis of individual components in aerosols may bring more constraints on the respective sources of pollution involved within the study area. The average carbon content in our aerosol samples was $40.54 \pm 0.09\%$, a relatively high value that may indicate that local air pollution results of coal combustion for heating purposes in the industry and communal sectors as well as of PM transport from surrounding areas. High inputs of carbon in PM has already been widely documented in Poland (e.g., Zimnoch *et al.*, 2020; 31.3–67.5% of TC in TSP) but also in Spain (e.g., Galindo *et al.*, 2019; 26% of TC in PM_{10} and 48% of TC in PM_1), Czech (Kucbel *et al.*, 2016; 26–39% of TC in PM_{10}) and even in more remote areas such as China (e.g., Xu *et al.*, 2015; ~20% of TC in $\text{PM}_{2.5}$ and ~30% of TC in $\text{PM}_{0.25}$). While the highest TC concentrations (in SM Table S1) were observed in samples older than 2012 (from 0.65 mg g^{-1} (location 11) to 2.68 mg g^{-1} (location 14), average of $1.48 \pm 0.64 \text{ mg g}^{-1}$), the lowest ones were measured in samples from 2013 (from 0.33 mg g^{-1} (location 11) to 1.01 mg g^{-1} (location 15), average of $0.72 \pm 0.18 \text{ mg g}^{-1}$; Table 1). Samples from 2012 presented intermediate contents (from 0.58 mg g^{-1} (location 12) to 2.37 mg g^{-1} (location 13), average of $1.28 \pm 0.53 \text{ mg g}^{-1}$; Table 1). The fact that the highest TC concentrations were measured in the oldest samples probably results of a longer exposure time to aerosol deposition. On the opposite, the year 2013 when the lowest TC concentrations were obtained, lasted only the period of the vegetative season and thus was expectedly only impacted by emissions from road traffic. For the years encompassed by our needle samples the Regional Inspectorate for Environmental Protection (WIOŚ) reported negligible variations in the levels of atmospheric PM for the Holy Cross Voivodship area, with levels that did not exceed the EU guidelines (WIOŚ, 2012, 2013, 2014). Hence, we can conclude that aerosol accumulation on needles is linked to the duration of exposure rather than to any increase in the pollution level over the same period, in agreement with Teper (2009), who also showed that the mass of the particles deposited on needles increases with their age.

The presence of OC in our samples could be associated with biogenic particles, volatile biogenic compounds from natural sources or with secondary processes taking place in the atmosphere (e.g., oxidation by O_3 , OH, NO_3 , NO_2 ; e.g., Kucbel *et al.*, 2016). The highest OC concentrations were observed in samples older than 2012, were slightly lower in 2012 and the lowest ones in 2013 (Table 1). As dust particles damage the needle wax layer, they inherently block stomata that damages needles' conditions, and ultimately lead to the intensification of fungal growth on their surface (Bačić *et al.*, 1999). The intensity of this fungi development is positively related to the needle exposure time to air pollutants (Teper, 2009). While we did not monitor the presence of fungi, Teper (2009) proved that a long exposure time can lead to the fast development of fungi and hence to an eventual increase in the OC concentrations. The largest OC difference we observed between the oldest and the youngest samples however corresponds to an exposition time that was too short to allow for an abundant development of fungi. Hence, in the oldest samples high OC may be associated with a large amount of biogenic particles accumulated over time on the surface of the needles. For the oldest samples (< 2012) the OC concentrations varied between 0.61 (location 11) and 2.65 mg g^{-1} (location 14), average of $1.48 \pm 0.64 \text{ mg g}^{-1}$; in 2012, from 0.47 (location 12) to 2.32 mg g^{-1} (location 13), average of $1.23 \pm 0.54 \text{ mg g}^{-1}$; and in 2013 from 0.33 (location 11) to 0.94 mg g^{-1} (location 15), average of $0.70 \pm 0.17 \text{ mg g}^{-1}$. Similarly to what we observed for the TC concentrations, the maximum OC values, for the three different periods, were measured for the exact same samples: sampling locations 14, 13, 15 for < 2012 , 2012 and 2013, respectively. This may indicate that within the total carbon pool, organic carbon (OC) represents the major reservoir.

On the other hand, elemental carbon (EC) concentrations did not exceed 0.2 mg g^{-1} , which indicates that EC contributed slightly to TC. This might be explained by the fact that EC is mostly contained in the fine fraction of the aerosols (Zhang *et al.*, 2020) that is less easily deposited compared to the coarse fraction. While diesel road traffic has been identified elsewhere as one of the major sources of EC (e.g., Bond *et al.*, 2013; Yamagami *et al.*, 2019) our highest EC concentrations were recorded during the heating season (one-year old samples; Fig. 7(B)), when emission from road traffic is not expected to dominate. During the heating season the generally high carbon concentration in the atmosphere are related to low temperatures and meteorological conditions that cause poor dispersion conditions that lead to the condensation of semi volatile species (Galindo *et al.*, 2019). Hypothesizing that i) diesel was a major source of EC and ii) the yearly road traffic was somewhat constant in the region, it was expected that EC concentrations would be similar over the different sampling periods. Results also indicated that EC concentrations differed between sampling location, and moreover seemed to increase with the needle exposure time to air pollution (Fig. 7). The highest EC concentrations were measured in aerosols deposited on needles corresponding to sampling locations 4 and 12, in needles older than 2012 (Fig. 7(C)). Sampling location 12 is on a peak, hinting that the high EC concentrations may be associated to long-distance air masses transport. For sample 4, the contamination seemed to be related to home heating from the nearby habitations, although road traffic may also be a non-negligible source of contamination. For samples with shorter exposure times (Figs. 7(A) and 7(B)) the highest EC concentrations were observed at sampling points 15 and 12, both located on peaks that may again indicate the impact of transboundary pollutants (i.e., incomplete fossil fuel combustion) from nearby industrial plants. Coal combustion from home heating may also contribute to the EC budget, but delineating its impact zone is somewhat difficult at this point.

Fig. 8 reports the covariations between $\delta^{13}\text{C}_{\text{TC}}$ and EC in aerosols deposited on the surface of our needle samples. Fields A, B and C delimit samples that were collected close to residential buildings (orange arrows, 3 and 4) and at elevated locations (blue arrows, 11 and 15) for different groups of needle samples (2013, 2012 and older than 2012, respectively).

Although we previously discussed the possibility that samples older than 2012 may be impacted by the accumulation of organic particles over time, results indicated statistically significant ($p < 0.05$) differences between 6-months-old samples (2013) and one-year-old samples (2012) (Fig. 8). Results in Fig. 8 show that for some needle samples we can observe noticeable differences between the different needles generations. For example, samples from locations 3 and 4 showed a combined increase in their respective EC concentrations and $\delta^{13}\text{C}_{\text{TC}}$ from 2012 to 2013 that can be interpreted as an increasing impact of emissions from home heating. For samples 11 and 15 (elevated areas) the signal probably corresponds to aerosol contamination transported from nearby urbanized areas.

Samples 9 and 10 have characteristics in Fig. 8 that are similar to those of fields D and E, representative of emissions from road traffic. Our results suggest that differences are only noticeable at sampling locations dominated by a single source of pollution. Interestingly, the $\delta^{13}\text{C}_{\text{TC}}$ values are increasing with age at location 10. As location 10 is closer to residential buildings, this trend might be explained by inefficient coal combustion, as an accumulation of coal soot ($\delta^{13}\text{C} = -24.5\text{‰}$) will increase the carbon isotope composition. In turn, samples at location 9 were collected right next to a busy road. Hence, the influence of diesel particles (-28.3‰) or unleaded fuel particles (-26.8‰) were clearly identified. For both fields D and E $\delta^{13}\text{C}_{\text{TC}}$ differences were observed between samples from 2012 and 2013: one-year-old samples (2012) were characterized by slightly more positive values than 6-months-old samples (2013); -30.2‰ (location 9), -29.0‰ (location 10) and -31.0‰ (location 9), -29.6‰ (location 10), respectively. This decrease in $\delta^{13}\text{C}$ between 2012 and 2013 may be explained by the fact that in 2013 the heating season signal was not preserved. Most terrestrial plants (C_3 plants) are characterized by $\delta^{13}\text{C}$ values ranging from -34‰ to -24‰ (Šturm *et al.*, 2012). Thus, the $\delta^{13}\text{C}$ of samples that only reflect the growing season will be more negative than those exposed for longer periods of time. Here, we observed more positive $\delta^{13}\text{C}$ values resulting of fossil fuel or biomass combustion in samples exposed for one or more years.

Additionally, to confront our conclusions we conducted a Principal Component Analysis. Results showed that the first 2 factors explained 84% (determined by a Scree test) of the observed variations among the variables: 58% for Factor 1 and 26% for Factor 2 (Table 3). The remaining 16% constituted a random noise that is not interpretable using this technique. Factor 1 positively

correlates aerosol, TC and OC concentrations, while Factor 2 is controlled by EC concentrations and $\delta^{13}\text{C}$. As Factor 2 yields a positive correlation between $\delta^{13}\text{C}$ and EC concentrations, it can be associated with the combustion processes whereas Factor 1 represents all other processes.

Fig. 7. Elemental carbon concentrations at the surface of needle samples. (A) 2013 samples, (B) 2012 samples, (C) < 2012 samples.

Fig. 8. Relationship between $\delta^{13}\text{C}_{\text{TC}}$ and elemental carbon (EC) in deposited aerosols. Fields A (2013), B (2012) and C (< 2012) correspond to samples collected close to residential buildings and at the Park's peaks. Fields D and E represent points located close to roads (9, 10). Arrows represent changes in the carbon isotope compositions between years 2012 and 2013 (orange for residential areas, blue for peaks). The typical $\delta^{13}\text{C}$ ranges for potential anthropogenic sources are taken from the literature.

Table 3. Results of the Principal Component Analysis. Statistically significant values are identified in bold.

	Factor loads (Varimax normalized rotation)	
	Principal Component Analysis Statistically important loads > 0.60	
	Factor 1	Factor 2
Aerosol concentration [mg g^{-1}]	0.91	0.13
TC [mg g^{-1}]	0.98	0.10
EC [mg g^{-1}]	0.41	0.68
OC [mg g^{-1}]	0.98	0.06
$\delta^{13}\text{C}_{\text{TC}}$	-0.10	0.90
Factor contribution [%]	58	26

Fig. 9. Factor scores obtained for the one-year old needle samples at the different sampling locations.

Fig. 9 reports the factor scores obtained for each sample along Factors 1 and 2. While factor scores ranging between -1 and $+1$ indicate an average intensity for the controlling process, values $> +1$ indicate that the process is dominating and inversely a value < -1 indicates that the process is not contributing. Results (Fig. 9) show that Factor 2, associated to combustion processes, dominates for samples collected on peaks (sampling locations 12 and 15) or high altitudes (sampling location 11). This is also true for samples collected nearby inhabited areas (sampling locations 3, 4 and 6). However, factor scores for Factor 2 in samples collected close to roads did not yield high values, which may indicate that among the combustion processes associated to this factor, road traffic is not the most contributing.

5 CONCLUSIONS

Here, we investigated and demonstrated that *Abies alba* needles are reliable bioindicators to identify sources of aerosol contamination for a given area. These bio-passive samplers help to avoid the use and maintenance of expensive automatic samplers in inaccessible areas where air quality monitoring is required. Here, we are proposing that, in areas where they grow, fir needles are a good air quality monitoring tool. This applies especially to mountains and woody areas where using specialized equipment is not possible or very difficult due to altitude, the lack of access to electricity or a limited access for people. Still, this method requires that the accumulated mass of particles deposited on the surface of the needles be quantified, as an excess can block the supracuticular chambers and alter the carbon isotope signal. Using the example of the Świętokrzyski National Park (Holy Cross Voivodship, Poland) our results show that the highest

$\delta^{13}\text{C}$ values were observed at locations that were: a) at high elevations, b) near inhabited areas and c) outside the park. Using a PCA approach we identified that combustion processes mostly control their carbon contents. Our study also demonstrates that one-year-old needles are the most reliable samples. While part of the aerosols deposited on the needles can be removed by wind or rain, combining carbon stable isotopes and geochemical analysis provides a reliable assessment of the aerosol mass and greatly helps identifying the major sources of air pollution. Our results identified emission from home heating, road traffic and transport from nearby urbanized areas as the major sources of pollution in the ŚNP. Finally, we do not recommend using needles older than one year due to a high accumulation of organic particles that inherently alters the information that could be retrieved about obtained air pollution. The analysis of TC/OC/EC and of SEM images suggest that for these older samples, interpretation is rendered difficult and imprecise. At the same time, it still arises the need for further studies, especially inter-comparisons with reference methods.

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SUPPLEMENTARY MATERIAL

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