CHARACTERISTICS OF PINE NEEDLES EXPOSED TO MULTI-SOURCE POLLUTION IN SILESIA: RADIOCARBON CONCENTRATION IN PINE NEEDLES AND ELEMENTAL ANALYSIS OF THE NEEDLES' SURFACE DEPOSITS

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ABSTRACT. We present here the analysis of the radiocarbon concentration and the components deposited on 2-year-old *Pinus sylvestris L.* needles collected in 2021, which were exposed to air contaminants for approximately two years. The needles were collected from seven sampling sites located near roads, households, and industrial factories in Silesia, the most industrialized part of Poland. The radiocarbon concentration was investigated using liquid scintillation spectrometry. Scanning electron microscopy and energy-dispersive X-ray spectroscopy were used to quantitatively analyze the elements deposited on the surface of pine needles. The depletion of the radiocarbon concentration in pine needles relative to clean air was observed at most of the investigated sites. Although it has been observed that in the research area, the fossil fuel CO_2 emission ranging from 0.4 to 3%, we cannot exclude that Suess effect may be underestimated due to biomass burning and mixing of the $^{14}CO_2$ origin from different sources. A significant amount of silicon, nitrogen, and sulfur was commonly found in samples, Metal elements of Ca, Fe, Al, Mg, and K were also present in most samples. Heavier elements of Fe and Ti were present in higher concentrations only in needles obtained from sites nearer to the heat and power plant in Łaziska Górne.

KEYWORDS: EDS, LSC, pine needles, pollution, SEM, surface characterization.

INTRODUCTION

Increasing anthropogenic carbon dioxide emissions into the atmosphere due to the combustion of large amounts of fossil fuel combustion has changed the local and global carbon cycle. The impact of these carbon dioxide emissions on the isotopic concertation in trees (tree rings and foliage) is evident (Suess 1955; Molnar et al. 2007; Hua et al. 2013; Pazdur et al. 2013; Baydoun et al. 2015; Ndeye et al. 2017). The physiological processes of trees, such as their photosynthesis rate and stomatal conductance, can be affected not only by carbon dioxide, but also by other air contaminants, gases, and dust associated with human activities, such as industrial processes, road transport, and low and high-stack emissions (Staszewski et al. 1994). The CO_2 produced during fossil fuel combustion contains no radioactive $^{14}CO_2$ (Suess 1955). On the other hand, there are some other sources of the CO_2, where $\Delta^{14}C$ values of the CO_2 can be higher than in current atmospheric background. For example the processes connected with soil CO_2 flux or combustion of biomass or the emission of $^{14}CH_4$ by factories can enrich ^{14}C in local atmosphere (Molnar et al. 2007; Gorczyca et al. 2013).The CO_2 enters pine needles through their pores and is incorporated into plants by photosynthesis. Investigations performed in 2012–2014 in Silesia (Sensuła et al. 2018, 2021) showed that in contrast to the expected Suess effect (Suess 1955), there was a higher radiocarbon concentration in the foliage and pine tree rings grown in the industrial forests of Silesia compared with the $^{14}C_{NH1}$ concentration in clean air, estimated based on data from Jungfraujoch (Hammer and Levin 2017).

In the current study, we attempt to verify whether these effects can still be observed and to determine the radiocarbon concentration in pine tree needles in a multi-source pollution area in Silesia. The aims of this study were to determine spatial variations in the carbon isotopic composition of pine needles and to analyze the components deposited on the foliage surface.

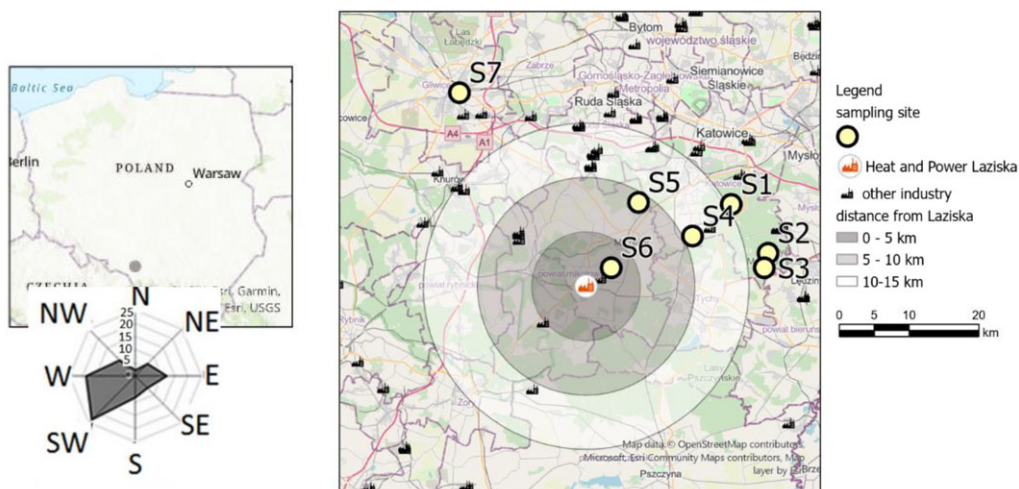*Corresponding author. Email: barbara.sensula@polsl.pl

Figure 1   Location of the sampling site and rose of the wind directions in Silesia. The spatial variation of the radiocarbon concentration of 2-year-old pine needles grown in seven sampling sites located near factories, roads, and households in Silesia. The samples were collected in April 2021. Distances of 5 km, 10 km, and 15 km from the heat and power plant Laziska have been marked.

Undertaken studies are a continuation of the authors' previous reports (Sensuła and Toroń 2019; Sensuła et al. 2019, 2020) presenting the elements deposited on pine needles in previous years. However, pine needles have been used as bioindicators since the end of the 20th century (Ericsson et al. 1989). They are used to specify the atmospheric pollution in other parts of Poland (Parzych and Jonczak 2014; Szwed et al. 2021), as well as all over the world e.g., in the Republic of Korea (Chung et al. 2021), Finland (Pöykiö and Torvela 2001), Croatia (Juranović Cindrić et al. 2019), Lebanon (Baydoun et al. 2015) and others. Data presented in this paper were compared to previously published research.

SEM (scanning electron microscope) imaging and EDS (energy dispersion X-ray spectroscopy) spectra were used to analyze the components deposited on the foliage surface. The working principle of electron imaging is based on de Broglie's theory and the Davisson and Germer experiment performed at the beginning of the 20th century (Goldstein et al. 2017). SEM and EDS are powerful techniques used in the analysis of sample surfaces. The primary electron beam interacts with the examined sample. Primary electrons can be scattered or absorbed in a sample volume in a depth of less than 100 nm up to 5 μm. The SEM image is created based on secondary electrons emitted from the sample, while specific X-ray emitted from the sample atoms allows estimating the elements present in the surface (Frankel and Aitken 1970). We have used these methods to visualize the leaf surfaces and quantify the atomic composition of pollutants. Pine needles have been used as bioindicators for more than three decades (Ericsson et al. 1989). This kind of research is currently performed worldwide to detect atmospheric pollution (Chung et al. 2021).

MATERIALS AND METHODS

Sampling

The sampling sites were located near the heat and power plant Łaziska (HPP Łaziska) in a multi-source pollution industrial area (Figure 1 and Table 1). Two of these sampling

Table 1 Sampling sites.

Site name	Commune/ Forestry	Longitude	Latitude	Distance to power plant (km)	Distance to the nearest industrial site (km)	Distance to the nearest road (km)
S1	Ochojec	19º1'58"E	50º12'0"N	15	2.7	0.7
S2	Ledziny I (Murcki Forest)	19º4'48"E	50º9'36"N	17	2.3	1.9
S3	Ledziny II (Murcki Forest)	19º4'30"E	50º8'53"N	16	3.7	0.8
S4	Podlesie	18º58'58"E	50º10'26"N	11	1.7	0.9
S5	Zadole	18º54'46"E	50º12'7"N	9	5.1	0.8
S6	Wyry	18º52'40"E	50º8'53"N	3	1.5	0.7
S7	Gliwice	18º40'58"E	50º17'31"N	21	2.1	0.2

sites were the same as those previously investigated in 2012–2014, where a high ^{14}C concentration in pine needles was observed (Sensuła et al. 2021).

In this study, seven sampling sites were located at different distances from factories, roads, and households, and six sampling sites in different communities (S1, S2, S3, S4, S5, and S6) were located 5 to 25 km from HPP Łaziska. One comparative site (S7) was located in Gliwice. The sampling sites were near streets and in direction of dominant winds. Samples of 2-year-old needles, which began growing in 2019, were collected in April 2021 on the same day- cloudy, not raining time, to avoid weather influences. In a comparative site, we collect two-year-old and one-year-old needles, which began growing in 2019 and 2020, respectively.

Radiocarbon

Needles were collected from the tree crowns, placed in plastic bags, and manually separated in the laboratory. The same standard protocol was used as previously during the analysis of the samples collected in 2012–2014 (Sensuła et al. 2015, 2021). The needles were lyophilized and prepared using a standard acid-alkali-acid treatment; thus, samples were converted to benzene according to the standard procedure used in laboratory (Pawlyta et al. 1998; Pazdur et al. 2013) for liquid scintillation counter (LSC) measurements. Determination of fraction of modern carbon ($F^{14}C$) and thus $\Delta^{14}C$ in pine needles was performed with a β-radiation liquid scintillation spectrometer (Quantulus 1220 type) (Pawlyta et al. 1998; Pazdur et al. 2013). The reference material ANU Sucrose (Rozanski 1991) was used. The average activity of the background and ANU sucrose standard activity was at the same level as presented in Sensuła et al. 2021.The $^{14}C_{NH1}$ concentration in clean air was estimated based on data from the monitoring station in Jungfraujoch, which was not affected by the local Suess effect (Emmenegger et al. 2021). In our approach, plant material was normalized to a $\delta^{13}C$ of –25‰ (Stuiver and Polach 1977). The measured ^{14}C concentration or activity was corrected and normalized to the standard of modern biosphere, resulting in the value of $F^{14}C$ (Reimer et al. 2004).

The $\Delta^{14}C$ value (‰), was calculated according to the following formula (Stuiver and Polach 1977, Mook and van der Plicht 1999; van der Plicht and Hogg 2006) method:

$$\Delta^{14}C = (F^{14}C \cdot e^{-\lambda(T_i - 1950)} - 1) \cdot 1000 \tag{1}$$

where: $F^{14}C$ – normalized radiocarbon concentration; λ – decay const ant for radiocarbon equal to 8267 yr^{-1}; T_i – calendar year of the samples collection).

The local Suess effect ^{14}S and fossil fuel CO_2 ($FFCO_2$) emission can be calculated and expressed as:

$$^{14}S = \frac{\Delta^{14}C_{bg} - \Delta^{14}C_{meas}}{\Delta^{14}C_{bg} + 1000} \, 100\% \tag{2}$$

$$FFCO_2 = \frac{CO_{2\,fossil}}{CO_{2\,meas}} = \frac{\Delta^{14}C_{bg} - \Delta^{14}C_{meas}}{\Delta^{14}C_{bg} + 1000} \tag{3}$$

where: $\Delta^{14}C_{bg}$ –background values of atmospheric CO_2; $\Delta^{14}C_{meas}$ – the local value of CO_2.

SEM and EDS Methods

The micrographs of pine needle surfaces were acquired by a scanning electron microscope (SEM; Phenom PRO X, Thermo Fisher Scientific). Based on the images, the clean-to-coated surface area ratio was estimated. The chemical composition of pollutants was investigated by energy-dispersive X-ray spectroscopy (EDS), which allows for the collection of secondary electrons within the energy range of 0.2–15 keV. ImageJ software was used to analyze the polluted surface area of pine leaves.

To ensure that SEM imaging and EDS analysis gave reliable information about the pollutants on the needle surfaces, the needle samples were collected from the forest and then placed in tubes and closed with sterile gauze to protect their surfaces from further contamination by human hands or the air in the laboratory. This also allowed water to evaporate freely from the tube, which protected the samples from mold growth. No further treatment was applied.

Surface area measurements were performed by ImageJ software and were used to calculate the coated leaf area ratio R_P as the ratio of the polluted area to the entire surface area:

$$Rp = \frac{A_P}{A_S} \cdot 100\%, \tag{4}$$

where A_P is the polluted area of pine needles, and A_S is the entire area of the needles.

RESULTS AND DISCUSSION

Radiocarbon

In the investigated highly-populated and industrialized region of Poland, where coal burning is the largest source of CO_2 emissions, a Suess effect is expected. In most of the sampling sites, this effect was noted. Each sampling site was located next to streets and not far from households and factories. Since trees absorb carbon dioxide from the atmosphere during photosynthesis through leaf stomata, a significant Suess effect in all investigated sites was expected. Figures 1 and 2 show that $\Delta^{14}C$ in the pine needles collected in 2021 was significantly lower than that of the samples collected in 2012–2014 (Sensuła et al. 2021). In 2021, in most of the investigated pines, the radiocarbon concentration was at a similar level (–10‰). A significantly lower value of $\Delta^{14}C$ (–30‰) was observed only in one location (S3), whereas a slightly higher ^{14}C concentration in pines relative to the ^{14}C concentration of clean air ($^{14}C_{NH1}$) was observed only in one site (S7). A relatively small decrease in $\Delta^{14}C$ in
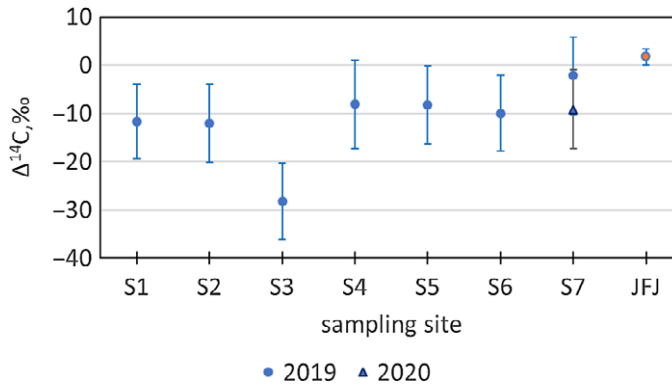
Figure 2 $\Delta^{14}C$ in 2-year-old needles grown in seven sampling sites (S1-S7) in the Silesia region near roads, households and in the air (JFJ-the reference value of the Jungfraujoch background), and factories, and a comparison to the fraction of modern carbon in 1-year-old needles grown near Gliwice (S7). The local Suess effect is noted in sampling site S3.

the pine needles relative to $^{14}C_{NH1}$ may be due to different local sources and origins of carbon dioxide. These include traffic, households, and industrial activities, as well as the combustion of biomass or the utilization of medical materials used as tracers (Sensuła et al. 2021). It has been observed that $\Delta^{14}C$ in the 2-year-old needles (which began growing in 2019) was lower than that of the one-year-old needles (which began growing in 2020). This effect was expected due to a decrease in $^{14}C_{NH1}$ and the loss of $^{14}CO_2$ containing artificially-produced ^{14}C atoms due to CO_2 exchange between different reservoirs of the Earth's carbon cycle. This was connected *inter alia* to dissolved CO_2 in oceans (Hua et al. 2013); thus, trees can be used in environmental biomonitoring applications.

The determination of foliage properties can be used to analyze local and regional environmental changes due to contaminants originating from different sources. The local Suess effect (^{14}S) is calculated to vary from 0.4 to 3‰ (at S3) (see Table 2), the median of ^{14}S value calculated from Equation (2) from the investigated area is ca. 1.2‰. However, we cannot exclude that the simplified formula of Equation (2) probably results in underestimation of the Suess effect for all investigated sites. Making the analysis of the carbon cycles and Suess effect according to the models (for example Turnbull et al. 2013) there are many different factors that simulates biological and physical processes controlling carbon cycles. That model has a set of 43 ecelogical parameters and take into account for example heterotrophic respiration, biomass burning, oceanic CO_2 sources, and nuclear-industry-produced ^{14}C. In Poland, there is no nuclear power plant, so the impact of the enrichment of atmospheric carbon dioxide in $^{14}CO_2$ from nuclear power plants (Molnar et al. 2007; Baydoun et al. 2015) in pine needles was neglected and we assume that there is no nuclear industry bias in our samples. Whereas, CO_2 emissions from biomass burning may play a significant role in Silesia. The biomass burning fraction is enriched in ^{14}C compared to the background, as the wood integrates ^{14}C over the lifetime of the trees. Wood has been used for heating the houses and coocking. Also biomass have been used in industrial sector. We cannot exclude the influence connected with recycling of the medical waste, where radiocarbon are used as markers. This is probably the reason, why the sample shows a similar value as Jungfraujoch: the fossil-fuel emission from this city (depleted in

Table 2   Carbon isotopic composition of the needles and Suess effect, fossil fuel emission of CO_2.

Site	$\Delta^{14}C‰$	$u(\Delta^{14}C)‰$	$^{14}S,\%$	$FFCO_2, ‰$
S1 (2019)	–11.7	7.7	1.3	13
S2 (2019)	–12.0	8.0	1.4	14
S3 (2019)	–28.2	7.9	3.0	30
S4 (2019)	–8.2	9.2	1.0	10
S5 (2019)	–8.3	8.1	1.0	10
S6 (2019)	–10.0	7.8	1.2	12
S7 (2019)	–2.2	7.9	0.4	4
S7 (2020)	–9.1	8.1	1.1	11

^{14}C) and the biomass burning emissions (enriched in ^{14}C) presumably compensate each other at least partially.

SEM and EDS Studies

SEM micrographs were analyzed to calculate the ratio of polluted areas. Figure 3 shows representative images and their EDS spectra for the most and least polluted sites. The contaminated surface areas differ for various needles. The amounts of pollutants on needle surfaces varied depending on the site, and some samples were significantly contaminated (Figure 3a), whereas others were covered with few pollutants (Figure 3b, 3c). The contaminants usually conglomerated and took the form of plate islands (Figure 3). In some cases, deposited pollutants covered the needles' stomata and were even invisible in the most polluted leaves (Figure 3a). The question arises whether only deposited contaminants influence the life functions of trees, or whether the mechanical blockage of stomata is also significant.

The ratio of the polluted surface (R_P) calculated for each sampling site is presented in Table 3. The area of pine needles obtained from the S7 reference site wascovered in the least. A comparison of the values obtained as a function of the radial distance from HPP Łaziska shows that the most polluted sites were located within 15 km of it (sites S4–S6), whereas areas further away were less contaminated (sites S1–S3). This effect is due to the height of the power plant chimney (162 m), so the pollutants travelled several kilometers in the air before depositing on the earth's surface, i.e., on pine leaves. Moreover, the contaminated sites were located southeast of the facility, which is consistent with the wind direction in southern Poland, which usually heads southwest in winter; therefore, this facility is one of the main pollutant sources in the examined area.

The qualitative and quantitative analysis of pollutants deposited on pine leaves was performed by using EDS. Figure 4 presents the elements recorded on the needle surface. Carbon and oxygen were not taken into consideration because it was not possible to determine whether the signals originated from cellulose or contaminants. Due to the EDS technique limitations, the contaminants with a contribution greater than 10% were recorded.

A significant amount of silicon was present in almost every sample, which may come from sand grains. N and S are also common pollutants, which probably come from their oxides. Ca, Fe, Al, and K elements were also present in most samples. Mg, N, and Ti (Figure 4) are
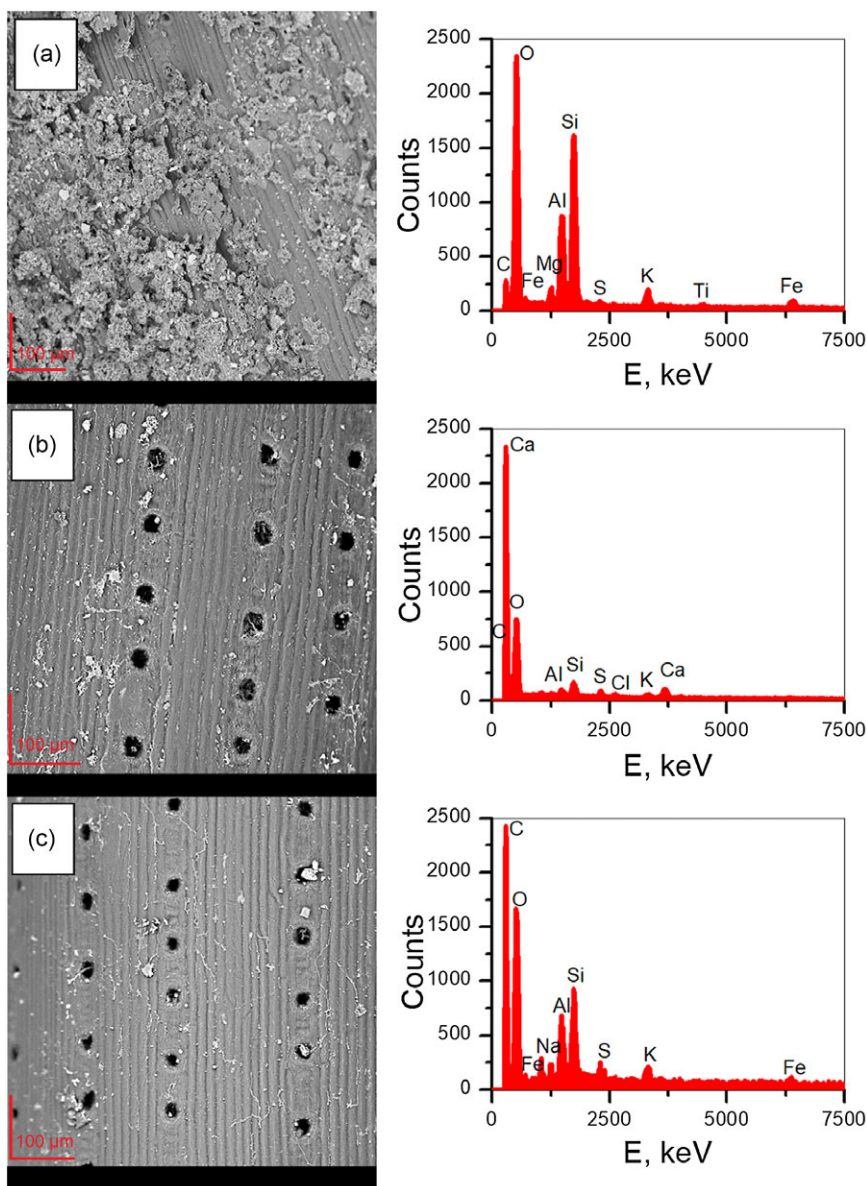
Figure 3   SEM micrographs and EDS spectra of pine needles obtained in 2019 from the S4 site, which was the most polluted (a), and those of the less-contaminated site S7 grown in 2019 (b) and 2020 (c). The peaks of specific elements are indicated.

also often deposited, but in much lower concentrations. Heavier elements such as Fe and Ti were present in higher concentrations in needles obtained from sites nearer to the heat and power plant in Łaziska Górne (S4–S6) than those obtained further from it (S1–S3). The weather conditions may influence the pollutants' concentration—rain or snow may rinse them off, but this impact should be similar for every site because of the long exposure time

Table 3   The ratio of the coated leaf area of pine needles grown in 2019 for each sampling site and those from the reference site (S7) collected in 2020.

Site	R_P, %
S1 (2019)	7.09
S2 (2019)	11.73
S3 (2019)	4.32
S4 (2019)	40.73
S5 (2019)	20.27
S6 (2019)	20.78
S7 (2019)	2.92
S7 (2020)	5.22
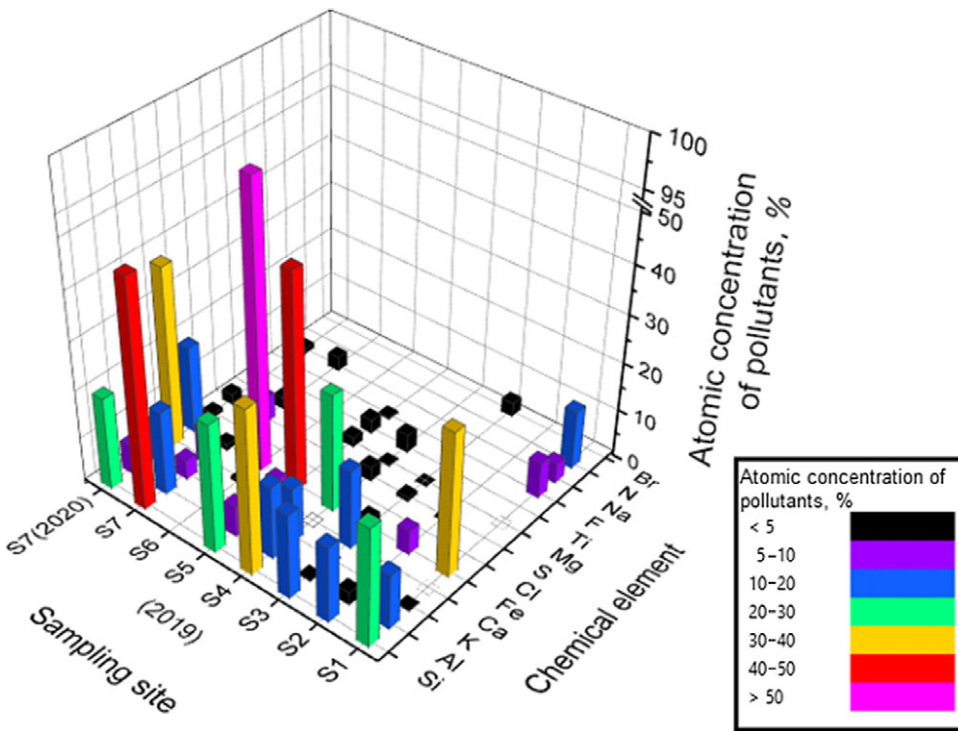
Figure 4   Atomic concentration of pollutants registered on the surface of *Pinus Sylvestris* L. needles grown in 2019 in selected sites and 2020 for the S7 reference site.

and nearly uniform weather conditions in the sampling area. For clarification, Table 4 presents the main elements in the pollutants determined from the EDS spectra.

Site S4 was also examined in our previous studies (Sensuła and Toroń 2019; Sensuła et al. 2019, 2020), which presented the elements deposited on pine needles in 2012 and 2013. Comparing these results shows that this site was more contaminated in previous years. Si, Al, K, Fe, S, Mg,

Table 4   Elements recorded on the surface of pine needles obtained from selected sites with an atomic concentration of pollutants greater than 10%.

Element	Pollutant contribution, %					
Site	Si	Al	K	Ca	Fe	N
S1 (2019)	25.40	12.28			30.82	13.25
S2 (2019)	16.65					
S3 (2019)	18.37			17.31		
S4 (2019)	34.83	16.07	12.43		25.41	
S5 (2019)	27.54				45.86	
S6 (2019)					97.74	
S7 (2019)	48.01	18.74				
S7 (2020)	20.13			38.43	19.13	

and Ti were detected in this study on the needle surfaces grown in 2019, while Ca, Cl, and N were also present in needles grown in 2012 and 2013. This may be because of the Covid-19 pandemic, during which a lockdown was implemented in almost all countries around the globe, which reduced the activity of pollutant-producing sources such as factories, heat and power plants, and traffic (Gope et al. 2021). For site S4, significant amounts of Al, Si, and K were found each sampled year, which indicates that these elements were present throughout the entire examined period. The estimated data are in good agreement with coal consumption and CO_2 emission by the power plant in Laziska obtained upon request from the Tauron company, which is the power plant owner and main power supplier in Poland. The coal consumption in the power plant was 1.536 Tg in 2019 and decreased to 0.888 Tg in 2020, while CO_2 emission was 3.027 Tg in 2019, and 1.774 Tg in 2020, respectively. The power plant in Łaziska is pure coal, however, one can keep in mind that the coal may be contaminated by some other chemical elements arising from mining and processing processes. Therefore, the proportional decrease of other pollutants may be expected.

High concentrations of As, Cu, Mn, Ni, Pb, Rb, and Sr were found on the surfaces of pine needles grown near an industrial complex and two urban parks in South Korea. The concentration of pollutants in some European countries has been established in several papers. The determination of sulfur and heavy metals in *Pinus Sylvestris L*. needles was studied in northern Finland in the Kemi neighborhood situated on the Gulf of Bothnia (Pöykiö and Torvela 2001). A paper industry complex is situated in the center of the examined area. It was stated there that pine leaves are suitable as bioindicators, especially for sulfur pollutants. In our samples, no significant amounts of sulfur were discovered. Several pine species, i.e., *Pinus densiflora Siebold et Zucc.*, *Pinus nigra Arnold*, *Pinus sylvestris L.*, and *Pinus thunbergiana Franco* were examined. The needles were collected from the Lisičine Arboretum, Croatia in 2012 (Juranović Cindrić et al. 2019). The authors examined 23 metals (Al, As, B, Ba, Ca, Cd, Co, Cu, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, and Zn) using spectrometric detection methods. Al, Ca, Fe, K, Mg, and Mn were detected in the highest amounts, and other metals were only present in trace amounts. Similar elements were detected by EDS on the pine needle surfaces in our studies.

It is valuable to compare identified elements found in our studies with the pollutants in other parts of Poland found by other researchers. Szwed et al. (2021) studied *Pinus sylvestris L.* needles grown in the southwestern part of the Świętokrzyskie Mountains in the Białe

Zagłębie region, Poland near a cement plant. They detected several metals using EDS, whose descending concentration was as follows: Al, Fe, Mg, Zn, Sr, Pb, Mn, Ni, Cr, Cu, Co, and Cd. Al and Fe were also found in our samples. In other studies (Parzych and Jonczak 2014), the Zn, Mn, and Pb were detected on *Pinus sylvestris L.* needles collected in the city of Słupsk in northern Poland.

No heavy metals and a scant amount of sulfur were detected in our research, in contradiction to cited works. This allows us to state that the attachment of chimney filters likely reduces environmental pollution in the industrialized Silesia region.

CONCLUSIONS

The main aim of this article is to present the results of the analysis of the components deposited on Pinus sylvestris L. needles, which were exposed to air contaminants and radiocarbon concentration in 2-years old needles. Sampling sites were chosen at a different distance from HPP Łaziska—the primary polluter in the neighborhood. In 2021, in most of the investigated pines, the radiocarbon concentration was at a similar level, only in one location a significantly lower value of $\Delta^{14}C$ (–30‰) was observed only in one location (Lędziny II), whereas a slightly higher ^{14}C concentration in pines relative to the ^{14}C concentration of clean air ($^{14}C_{NH1}$) was observed only in one site (Gliwice). It can be due to different local sources nad origins of carbon dioxide. The median of ^{14}S value in the investigated area is ca. 1.2%. Comparing radiocarbon concentration in 1-year-old and 2-year-old pine needles growing in the same sampling sites it has been observed that $\Delta^{14}C$ in the 2-year-old needles (which began growing in 2019) was lower than that of the one-year-old needles (which began growing in 2020). This effect was expected due to a decrease in $^{14}C_{NH1}$ and CO_2 exchange between different reservoirs of the Earth's carbon cycle. It was found that the most polluted sites were located within 15 km of it, whereas areas further away were less contaminated. N, S, Ca, Fe, Al, and K were commonly detected. Fe and Ti were also present in the samples collected from sites nearer to the HPP Łaziska. The impact of the Covid-19 pandemic and implemented lockdown is also visible. The decrease in coal consumption in 2020 by about 50% compared to 2019 resulted in lower pollution. No heavy metals and a scant amount of sulfur were detected in our research, which emphasizes the importance of chimney filters in reducing the environmental pollution.

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REFERENCES

Baydoun R, Samad O, Nsouli B, Youness G. 2015. Seasonal variations of radiocarbon content in plant leaves in a ^{14}C depleted area. Radiocarbon 57(3):389–395.

Chung, D, Lee, J-H, Lee, S-Y, Park, K-W, Shim, K-Y. 2021. Efficacy of pine needles as bioindicators of air pollution in Incheon, South Korea. Atmospheric Pollution Research 12(5):101063. doi: 10.1016/j.apr.2021.101063.

Emmenegger, L, Leuenberger, M, Steinbacher, M, ICOS RI, 2021. ICOS ATC/CAL 14C Release, Jungfraujoch (10.0 m), 2016-01-04–2019-08-12, https://hdl.handle.net/11676/JjmhH4pUyWlbqTA Ax4x54deg.

Eriksson, G, Jensen, S, Kylin, H, Strachan, W. 1989. The pine needle as a monitor of atmospheric pollution. Nature 341:42–44. doi: 10.1007/s137 62-018-2096-x.

Frankel RS, Aitken DW. 1970. Energy-dispersive X-ray emission spectroscopy. Applied Spectroscopy 24(6):557–566. doi: 10.1366/00037027077437 2308.

Goldstein, JI, Newbury, DE, Michael, JR, Ritchie, NWM, Scott, JHJ, Joy, DC. 2017. Scanning electron microscopy and X-ray microanalysis. New York: Springer.

Gope S, Dawn S, Das SS. 2021. Effect of COVID-19 pandemic on air quality: a study based on air quality index. Environmental Science and Pollution Research 28:35564–35583. doi: 10.1007/s11356-021-14462-9.

Gorczyca Z, Kuc T, Różański K. 2013. Concentration of radiocarbon in soil-respired CO_2 flux: data-model comparison for three different ecosystems in southern Poland. Radiocarbon 55(2–3):1521–1532.

Hammer S, Levin I. 2017. Monthly mean atmospheric $^{14}CO_2$ at Jungfraujochand Schauinsland from 1986 to 2016 [data set, www document]. University Library Heidelberg. doi: 10.11588/data/10100.

Hua Q, Barbetti M, Rakowski AZ. 2013. Atmospheric radiocarbon for the period 1950–2010. Radiocarbon 55:2059–2072.

Juranović Cindrić I, Zeiner M, Starčević A, Stingeder G. 2019. Metals in pine needles: characterisation of bioindicators depending on species. International Journal of Environmental Science and Technology 16:4339–4346. doi: 10.1007/s13762-018-2096-x.

Molnár M, Bujtás T, Svingor É, Futó I, Světlík I. 2007. Monitoring of atmospheric excess ^{14}C around Paks nuclear power plant, Hungary. Radiocarbon 49:1031–1043.

Mook W, van der Plicht J. 1999. Reporting ^{14}C activities and concentrations. Radiocarbon 41(3):227–239.

Ndeye M, Sene M, Diop D, Saliege JF. 2017. Anthropogenic CO_2 in the Dakar (Senegal) urban area deduced from C-14 concentration in tree leaves. Radiocarbon 59(3):1009–1019.

Parzych A, Jonczak J. 2014. Pine needles (*Pinus Sylvestris* L.) as bioindicators in the assessment of urban environmental contamination with heavy metals. Journal of Ecological Engineering 15(3):29–38. doi: 10.12911/22998993.1109119

Pawlyta J, Pazdur A, Rakowski AZ, Miller BF, Harkness DD. 1998. Commissioning of a Quantulus 1220^{TM} liquid scintillation beta spectrometer for measuring ^{14}C and ^3H at natural abundance levels. Radiocarbon 40(1):201–210.

Pazdur A, Kuc T, Pawełczyk S, Piotrowska N, Sensuła BM, Różański K. 2013. Carbon isotope composition of atmospheric carbon dioxide in southern Poland: imprint of anthropogenic CO_2 emissions in regional biosphere. Radiocarbon 55(2–3):848–64

Pöykiö R, Torvela H. 2001. Pine needles (*Pinus Sylvestris*) as a bioindicator of sulphur and heavy metal deposition in the area around a pulp and paper mill complex at Kemi, northern Finland. International Journal of Environmental Analytical Chemistry 79(2):143–154. doi: 10.1080/03067310108035906.

Reimer PJ, Brown TA, Reimer RW 2004. Discussion: reporting and calibration of post-bomb ^{14}C data. Radiocarbon 46(3):1299–1304.

Rozanski K. 1991. Consultants' group meeting on ^{14}C reference materials for radiocarbon laboratories. February 18–20, 1991, Vienna, Austria. IAEA Internal Report. Vienna: International Atomic Energy Agency.

Sensuła B, Fagel N, Michczyński A. 2021. Radiocarbon, trace elements and Pb isotope composition of pine needles from a highly industrialized region in southern Poland. Radiocarbon 63(2):713–726. doi: 10.1017/RDC.2020.132.

Sensuła B, Michczyński A, Piotrowska N, Wilczyński S. 2018. Anthropogenic CO_2 emission records in Scots pine growing in the most industrialized region of Poland from 1975 to 2014. Radiocarbon 60(4):1041–1053. doi: 10.1017/RDC.2018.59.

Sensuła B, Toroń B. 2019. Bio-monitoring of the industrial forest area nearbay Łaziska Power Station (Poland): distribution of the contamination of the surface of the scots pine needles. In: Wójtowicz, AA, Marciszuk, K, editor. European Society for Isotope Research Isotope Workshop XV. ESIR 2019, Lublin, Poland, June 23–27, 2019. Book of abstracts. Warsaw: Polish Geological Institute – National Research Institute. p. 137–143. Available online: https://esir.org.pl/2019/ESIR2019_big.pdf.

Sensuła B, Toroń B, Piotrowska N. 2019. Scanning electron microscopic analysis of trace elements

deposition on the pine foliage. In: Adamiec G, Pazdur A, Michczyńska D, Poręba G, editors. Methods of absolute chronology. 13th International Conference, 5–7 June 2019, Tarnowskie Góry, Poland. Abstracts and programme. Gliwice: Institute of Physics – CSE. Silesian University of Technology. p. 118–119.

Sensuła B, Wilczynski S, Opala M. 2015. Tree growth and climate relationship: dynamics of Scots pine (*Pinus Sylvestris* L.) growing in the near-source region of the combined heat and power plant during the development of the pro-ecological strategy in Poland. Water Air and Soil Pollution 226(7), article 220.

Sensuła B, Wilczyński S, Toroń B, Piotrowska N. 2020. Biomonitoring obszarów przemysłowych Śląska—zastosowanie metod dendrochronologicznych, spektrometrycznych i mikroskopowych w badaniach drzewostanów sosnowych w pobliżu elektrociepłowni w Łaziskach Górnych. In: Pikoń K, Bogacka M, editors. Współczesne Problemy Ochrony Środowiska i Energetyki 2019. Gliwice: Katedra Technologii i Urządzeń Zagospodarowania Odpadów. p. 131–135. (in Polish) Available online: https://drive.google.com/file/d/1YGxjDGRhAvJFOh-VX63lH-FETLHJmsD1/view.

Staszewski T, Godzik S, Poborski P. 1994. Physico-chemical characteristics of pine needle surfaces exposed to different air pollution sources. In: Percy KE, Cape J, Jagels R, Simpson CJ, editors. Air pollutants and the leaf cuticle. Berlin: Springer. p. 341–349.

Stuiver M, Polach H. 1977. Discussion: reporting of ^{14}C data. Radiocarbon 19:355–363.

Suess HE. 1955. Radiocarbon concentration in modern wood. Science 122(3166):415–7

Szwed M, Żukowski W, Kozłowski R. 2021. The presence of selected elements in the microscopic image of pine needles as an effect of cement and lime pressure within the region of Białe Zagłębie (central Europe). Toxics 9:15. doi: 10.3390/toxics9010015.

Turnbull J, Keller E, Baisden T, Brailsford, G, Bromley, T, Norris, M, Zondervan A. 2013. Atmospheric measurement of point source fossil CO_2 emissions. Atmospheric Chemistry & Physics Discussions: 14,501–15,014.

van der Plicht J, Hogg A. 2006. A note on reporting radiocarbon. Quaternary Geochronology 1(4): 237–240.