Tree Bark, a Valuable Source of Information on Air Quality

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Abstract

Tree bark has been proven to be a valuable source of information on air pollution. Bark has a large absorbent surface thanks to its deeply furrowed structure. Through the ability to accumulate atmospheric particulate matter (PM), tree bark enables the identification and mapping of organic and inorganic air pollutants. The first study of air quality using tree bark dates back to the second half of the 20th century and such studies are constantly being developed today. Reports published almost every year present the potential of using tree bark of different tree species for monitoring atmospheric pollution. This article presents scientific evidence proving the possibility of using bark in the process of assessing air quality and also describes the main directions of research in this field.

Keywords: air pollution, bioindication, air monitoring, tree bark, elemental analysis

Introduction

Human activity has resulted in an increased release of contaminants into the environment. The atmosphere is the element of the environment that is particularly vulnerable to contamination by substances of human origin [1-5]. Because of continuous mixing of air masses in the atmosphere, contamination can affect areas far from the emission source. In the words of A. Kalinowska (1994), "The wind does not stop at national borders, and pollutants do not spread fairly" [6]. Cross-border transmission of air pollutants makes it impossible for the problem of air quality to be considered in local terms only. Close international cooperation in the monitoring and prevention of air contamination is necessary, and not limited to geographical regions or continents, but covering the whole world [2, 7-11].

Air pollutants are substances defined mainly as unnatural constituents of the air and also those naturally occurring in the atmosphere, but at concentrations much higher than standards. Among the contaminants of anthropogenic origin in the air one can distinguish gaseous components and solids (dust) [4]. Gaseous air pollutants include organic and inorganic compounds, e.g., carbon oxides (CO, CO_2), sulphur dioxide (SO_2), nitrogen oxides (NO_x), or volatile organic compounds (VOCs), whereas solid air pollutants refer to the particulate matter (PM) in the form of ash, soot, dust, cement, or metallurgical dust. Falling dust that contains, for example, metal oxides permanently contaminates other elements of the environment [7, 12-14]. The long-term impact of air pollution consequently results in the impoverishment of biodiversity and reduction of vitality in all ecosystems. Harrison and Yin (2000)

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identified several compounds of airborne PM, possibly toxic to living organisms, including the following: bulk chemical compounds, trace elements, strong acids, and sulphates [7]. A direct correlation between air quality and the incidence of respiratory diseases in humans has been proven [7-8, 15-16]. Air pollution is considered to be the single largest cause of environmental risk nowadays, and this relationship is also confirmed by the World Health Organization [17]. Although it is assumed that anthropogenic dust represents only 3% of global PM, the substances introduced by human activity may cause far-reaching and unpredictable changes in the environment [14]. A particular threat to all ecosystems is trace elements, including the heavy metals found in dust pollution. The natural content of metals in the environment is relatively low, so that their excessive emissions into the atmosphere can result in their accumulation in the trophic chain, which in turn contributes to biosphere degradation at every organizational level [18-19].

In order to assess the potential risks arising from air pollution by foreign substances, the most popular are physicochemical tests. Nevertheless, in contrast to physicochemical monitoring that provides information only about air pollution at the time of measurement, biomonitoring using living organisms provides comprehensive data on impurities accumulation in the environment for long periods of time [10, 20]. Plants are particularly sensitive to changes in the air and are widely used in air monitoring. Assessing air quality based on plants can be done using two methods: analysing impurities accumulated by the plant and using the plant to observe changes (usually unfavourable) in the morphology or physiology of plants caused by pollutants, thus related to ecotoxicology [13, 19-20]. In a study of air quality, lichens and mosses are the most frequently used bioindicators, individual species of which can point directly to the degree of contamination, and special scales have been developed for such species [1, 21-28]. Mosses and lichens may occur in all studied locations, but higher plants are often selected as suitable bioindicators.

Higher plants are not capable of capturing atmospheric pollution as easily as mosses and lichens. Accumulation of air pollution by higher plants is mainly the result of adsorption (deposition on terrestrial parts). The use of higher plant organs in the monitoring of air pollution is practically a form of bioindication consisting mainly of studying the physiological effect of pollution (yellowing, shedding needles and leaves, deformation of limbs, disturbance of flowering or fruiting, loss of bark elasticity) [19-20, 29-32]. Among the higher plant organs, leaves have proven to be particularly useful in air monitoring. Since contamination settling on leaves can easily be removed by wind or washed away by precipitation (acid rain can leach alkaline cations), this method does not provide conclusive results regarding air pollution in an area and can even deliver false results [4, 33-35]. Odabasi et al. (2016) distinguished the three most effective pathways of contaminants entering the plant. Besides uptake by the roots, contaminants can penetrate the plants through dry deposition on leaf and absorption through bark surfaces [11]. In recent years, the use of tree bark is becoming more and more popular for determining air pollution results [4, 35] This article presents the current state of knowledge regarding the possibility of using tree bark as a bioindicator of historical and cumulative air pollution.

General Structure of Tree Bark

Bark is commonly known as a uniform cover and the outer layer of trunks of trees and woody shrubs. However, what generally is considered to be bark is in fact an imprecise concept referring only to the outermost parts of its structure. Indeed, bark consists of layers made of a number of tissues of different origin. In the overall structure of so-called bark, there are only two meristematic regions capable of cell division: the cork and the vascular cambium. The outermost, cracked, and irregular outer layer called cork (*fellem*) is a secondary tissue arising from outward intense divisions of meristematic cells in cork cambium (*phellogen*). Cork cells are dead, and their cell walls contain suberin, a substance composed of long-chain fatty acids that provide protection against moisture loss, among other things. Inward-dividing phellogen cells result in the formation of a thin layer of live parenchyma cells. This secondary layer of inner cells is called *phelloderm*. Owing to cambium activity, cork and *phelloderm* together form a secondary tissue cover called periderm. Besides periderm, in the innermost layers of bark there is secondary phloem emerging from divisions of vascular cambium. The living cells of this non-homogeneous tissue are involved in the transport of organic nutrients. Thus bark, as shown in Fig. 1, consists of two layers: the external periderm layer and the inner layer of secondary phloem [2, 36-37].

Bark is an organ of specific, cracked structure characteristic to the species. As an aboveground part of the plant, it is constantly exposed to weather factors (Fig. 1). The folded structure of bark gives it a relatively high specific surface area. A large surface area of bark with its large sorption capacity makes it able to stably adsorb dust suspended in the air, thus showing even small changes in the environment [2, 4, 26, 29-31, 35, 38-41]. Studies have confirmed that the sorption ability of bark varies significantly, depending on whether it is smooth or wrinkled [8, 13, 34]. Regardless of the physical properties, the factor in favour of the use of bark in monitoring air quality is its wide availability throughout the year. In addition, bark must meet certain criteria to provide clear and comparable measurement results. First of all, bark must be obtained from a species common in the area and having a well-known biology, and thus a large number of samples can be collected. Sampling should be performed in such a way as to be able to obtain clear environmental dependence. Thus, bark samples for research from a given area should be collected from specimens of the same species at a similar age as determined by measuring tree height and circuit diameter at chest height [19-20]. Furthermore, an important argument for using bark in air
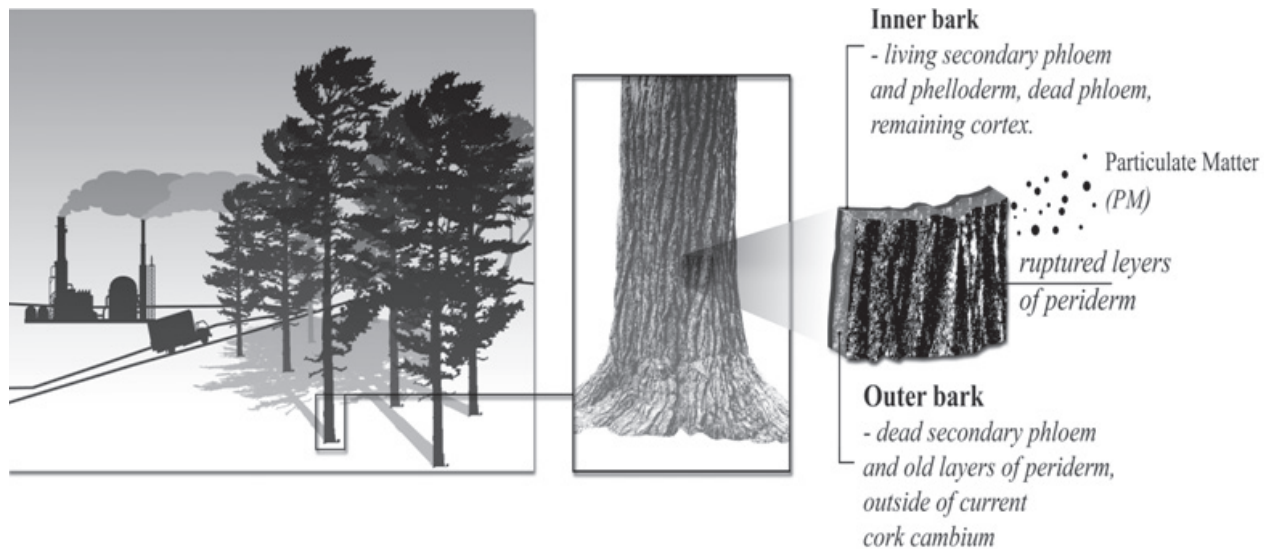
Fig. 1. Tree bark exposure to harmful factors originating mainly from industry and transport; the two-layer structure of the bark makes the impurities contained in the particulate matter deposit only on its outer, dead part.

monitoring is the lack of sampling influence on tree health status [26, 29-30].

Results and Discussion

Usefulness of the Tree Bark in Monitoring of Air Pollution

Evaluation of Inorganic Air Pollutants Using Tree Bark

The first studies on the use of tree bark in monitoring environmental changes were carried out in the second half of the 20th century. The study of air quality conducted on lichens proved that along with lichen samples, tree bark as a substrate should also be collected and treated as a sample. However, initial research was based on the observations of symptoms that the bark of many species showed under the influence of air pollution. The impact of atmospheric pollution is manifested, e.g., in the flaky falling off bark of *Fagus sylvatica* and *Acer pseudoplatanus*, and total loss of bark has been recorded with the elm (*Ulmus* sp.) [20].

The period between the 1960s and the 1980s brought a new line in research of air quality using tree bark. A special contribution in promoting the use of tree bark in air quality monitoring in this period can be attributed to Krystyna Grodzińska, whose work presenting tree bark as a bioindicator of air pollution caused quite a stir in the scientific world. This constituted an assessment of environment acidification by SO_2 from transport and industry on the basis of pH of the plant material tested [21, 29-30, 42-43]. At that time, a relationship was found between pH measurements of bark extracts and gaseous air pollutants, rich in acidic compounds (e.g., SO_2), coming from nearby transport routes (traffic pollution) or industrial emitters (industrial heavy metal surveys) [20,

44]. The relationship between the concentration of SO_2 in the atmosphere and acidity of the bark of many species was confirmed in studies on bark of such species as *Quercus robur*, *Tilia cordata*, and *Pinus sylvestris*. The results of the research showed, among other things, that the bark of deciduous trees had lower natural acidity than the bark of conifers, making the former potentially more sensitive biomarkers. In subsequent years, further investigation revealed a correlation between SO_2 concentration in the atmosphere and sulphur content from the settling dust in bark. Assessment of air pollution based on a study of bark acidity showed the latter to be sensitive only to large amplitude fluctuations in SO_2 concentrations in the air. On the other hand, determination of electrolytic conductivity of bark extracts proved to be a much more sensitive method even with small changes in SO_2 and CO_2 emissions into the atmosphere [20, 31, 43-44]. Notwithstanding, determining bark acidity is a still popular and inexpensive method for studying air pollution in areas subjected to strong human pressure. Studies conducted by Stainor et al. (2011) on the acidity of a four-species bark, including reports on black locust and European yew [45] as well as horseradish (2015) [32] that expand on the results of Grodzińska (1977, 1979) regarding the pH value of Scots pine bark in response to environmental conditions near Krakow [29-30], confirmed the possibility of the use of acidity of tree bark as an indicator of air pollution by acidic oxides of anthropogenic origin.

Elemental Analysis of Tree Bark

Apart from using tree bark to monitor changes in "typical" air pollutants (SO_2, NO_x), another group of researchers began to focus on the evaluation of the content in bark of heavy metals emitted by anthropogenic sources [1, 20]. The idea of holistic multi-elemental analysis of the plant material dates back to the turn of the 1970s and 1980s,

when it was noted that a linear relationship between the content of elements in the plant material and their contents in the environment existed [43, 46-47]. Initially, in studies involving bark, attention was focused only on impurities adsorbed on its surface in bark pockets. It was thought that adsorption on the bark surface (on dead plant material) was the only method of air pollution accumulation. It is now known that the analysis of element content in bark provides information about the levels of both air and soil pollution [20, 33-34, 39, 48]. This is because bark consists of the outer (dead) part, passively adsorbing air pollution, and the internal (live) part, absorbing pollution through the root system, straight from the soil (Fig. 1). Moreover, the elements can be sorted with increasing capacity to move from roots to shoots. Metals such as Cu and Pb show much lower mobility of this matter than Tl and Cd. On this basis it can be inferred that the large average content of less mobile elements (Co, Cr, Cu and Pb) in tree bark may come from air pollution. On the contrary, the source of bark pollution caused by highly mobile metals (Cd and Zn) is more difficult to identify unambiguously [18, 33-34, 49]. The two-layer structure of tree bark causes a lot of problems with the interpretation of results. Since the contribution of the inner part of bark to the total content of elements in bark is relatively small, it has been neglected by most authors [2, 4]. However, recent studies suggest a significant gradient of concentration of the elements within the layers of the bark. Janta et al. (2016) reported that concentrations of some metals, including Cr, Cu, Pb, and Zn, were highest in the cork layer of *Cassia fistula* bark, decreased in the second and third layers (phloem), and increased in the innermost layer (vascular cambium) [37]. Similar patterns of content gradients were observed for Hg in *Pinus nigra* bark [41].

It can be noted that since the late 1970s [46-47], elemental analysis of tree bark has been the primary direction in the study of air quality based on tree bark as a biological material. Almost every year scientific reports present the possibility of using the bark of other trees, previously not described for biomonitoring, in the effective monitoring of trace elements released into the atmosphere. Scientific reports predominantly refer to determination of the elemental composition of tree bark from urban agglomerations (both traffic and agglomeration air pollution) [4, 11, 26, 31, 33-34, 38-40, 46-58], but also from industrial emitters (industrial air pollution) [2, 8, 13, 59]. Multi-elemental analysis of the tree bark was recently used for determining air quality in Brazil in urban areas of Paranaguá [10] and São Paulo [60], Chiang Mai in northern Thailand [37], and in Italy's Liguria region [9, 35]. Considering pollution from industrial emitters, metallurgical industry sites are particularly troublesome "hotspots" of pollution emission into the atmosphere. Metals accumulate in the environment, which causes their practical non-degradable character. Bellis et al. (2003) proved that the bark of Japanese oaks can be suitable for monitoring the historical change in atmospheric arsenic deposition in the vicinity of industrial sites [61]. Also in the areas of mining, recent studies of Chiarantini et al. (2016) have shown that black

pine bark can be successfully used to determine air pollution by mercury compounds [41]. Research conducted by Conte et al. (2016) confirmed the possibility of using the bark of the Slippery Elm tree to detect uranium from nuclear fuel [14].

Especially valuable information on the possibility of using tree bark in bioindication was provided by studies conducted on large areas, countries, or geographical regions. Among the extensive research on the elemental composition of tree bark the work of Wolterbeek et al. (1996) conducted throughout the entire Netherlands (123 locations) regarding oak bark [62], among other materials, should particularly be noted, as should the study that Bohm et al. (1998) carried out in the western Czech Republic (457 locations) concerning multi-elemental analysis of oak bark [1]. Extensive research was conducted in Germany by Schulz et al. (2000) on the bark of Scots pine (273 locations) [63-64] and in Portugal by Pacheco et al. (2001, 2002) on the bark of olive trees (28 sampling sites) [65-66] and plane tree (2008) transplants in a mixed environment [65]. Saarela at al. (2005) [68] conducted multi-elemental analysis on the bark of birch, spruce, and Scots pine in southwestern Finland, a reference to the research carried out almost 10 years earlier by Poikolainen (1997) [44].

Tree bark as a biological material contains in its structure many trace elements whose content is variable in time and can therefore act as a selective filter for some elements, artificially increasing or decreasing the contents. The natural content of elements in the cortex, referred to as the bark matrix, can affect the results [5, 20, 39, 55]. Studies of Cantion et al. (2009, 2012) on the anthropological fraction of impurities deposited on bark show that bark may indeed respond as a selective filter, increasing or excluding certain elements, e.g. Ca, K, or Fe [33-34]. Also, studies on the adsorption ability of maritime pine bark confirm that the bark can act as a selective filter of heavy metals [55]. Therefore, in order to determine the influence of actual environmental pollution based on the elemental composition of tree bark, the natural level of elements in bark must be taken into account with awareness of possible interactions between the elements in bark and in dust. Furthermore, the elemental composition of bark also depends on the dryness of wet deposition. In contrast to studies based on leaves and other above-ground plant organs, the location of bark effectively prevents rainfall from washing away impurities absorbed on the surface [2, 5, 13, 33-34, 39, 63].

Although the bark of trees is a good natural sorbent of air pollution rich in trace elements, assessment of air quality should not be based only on studying the elemental composition of bark. Many trace elements present in air pollution (such as Al, Fe, Cr, Ni, or As) may both derive from natural sources and be emitted through human activity. The method of bark elemental analysis does not enable us to fully distinguish between natural and anthropogenic pollution and, even more, using this method it is not possible to distinguish between various sources among anthropogenic emissions [1, 8, 52-53]. Recent studies with

pine bark suggest the possibility of using lanthanide (La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb) to investigate industrial emissions [11]. However, a newer research approach to identifying contaminants and their emitters is to determine isotope ratios in the studied materials [27, 38]. Isotopic studies can be used to determine the origin of the elements in the atmosphere. Due to increased transport and industrial development, Sr, Nd, Pb, and U isotopes are of particular importance in environmental studies, also successfully determined in tree bark [39, 53, 69]. Also, stable isotope ratio analysis of C, N, and O (^{13}C, ^{18}O, and ^{15}N) can be successfully used as long-term indicators of environmental changes according to Cocozza et al. (2016) [5]. Recent studies related to the content of the isotope concerned ^{137}Cs in the bark of mainly oak and spruce. ^{137}Cs in the atmosphere comes from nuclear tests and also from the 1986 nuclear disaster in Chernobyl. Studies have demonstrated the highest content of ^{137}Cs in oak bark, which can be a promising long-term indicator of contamination of this isotope [70]. Apart from isotopes, tree bark may also provide information relating to element speciation and degree of oxidation. Studies of Mandiwana et al. (2006) demonstrated the possibility of using acacia bark as a bioindicator of toxic hexavalent chromium Cr (VI) in air pollution in South Africa due to the high accumulating ability of bark for chromium from air dust [59].

Evaluation of Air Organic Pollutants Using Tree Bark

In terms of chemical structure, pollutants in the atmosphere can be divided into organic and inorganic compounds [7]. Inorganic contaminants are represented by oxides and heavy metals described above. Organic contaminants are a fixed group composed of substances that can easily pass in the form of vapour or gas and have low water solubility. The general name of organic compounds in the atmosphere is volatile organic compounds (VOCs). These compounds, such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organobromine compounds, or dioxins, include, besides the carbon backbone chain, oxygen, hydrogen, fluorine, chlorine, sulphur, nitrogen, or bromine in their structure. Many organic pollutants are dangerous to the environment due to their resistance to degradation in natural conditions, hence the term POPs (persistent organic pollutants). Organic compounds from anthropogenic sources are never present in the environment individually, but always as multi-component mixtures of varying compositions. Many of the organic compounds emitted into the environment have a detrimental impact on the biosphere. Toxicity and even certain carcinogenicities of some of them have been proven. It is still not fully known how they interact in mixtures with other types of pollutants. Therefore, monitoring POPs emitted into the environment seems to be extremely important [12, 25, 50, 71-81].

Studies of organic pollutants from the air using bark were initially limited to the determination of polyaromat-ic hydrocarbons. PAHs are a large organic group of compounds that occur in both gas phase and solid air pollution. Although about 100 different PAHs are known, only 17 are present in the environment – with at least two fused aromatic rings being the basis of their chemical structure. Many PAHs exert toxic and even carcinogenic effects on humans, e.g., benzo(a)pyrene. The study of air quality based on, among other things, pine bark [25, 74, 76] or camphor [77] in both urban and industrial environments has proven that tree bark can be successfully used to assess the spatial distribution of ambient air PAHs. In a study by Rauert and Harner (2016), authors analyzed the bark of 5-15-year-old red pines and divided PAHs into fractions: alkylated-PAHs, nitro, and oxy-PAHs. The results showed a trend of spreading of POPs confirming the usefulness of the bark to evaluate historical air pollution [81]. Furthermore, bark is able to capture PAHs from the air as well as from commercial filters, e.g., polyurethane foam samplers (PUFs), which is confirmed by a study of Li et al. (2016) [80].

Relatively recently, tree bark has been used as a passive air indicator for organic compounds, including dioxins (e.g., polychlorinated dibenzofurans, PCDFs, or dibenzo-p-dioxins, PCDDs), polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs), chlorinated pesticides, and ammonium nitrate [25, 58, 73, 78, 82-83]. Research conducted by Gueguen et al. (2011) [12] as well as Salamova and Hites (2012) [84] indicates that tree bark is a particularly sensitive indicator of organobromine compounds: PBDEs (polybrominated diphenyl ethers) and PCBs. However, having a long life cycle, tree bark consequently can accumulate pollutants over a significant amount of time. Hermanson and Johnson (2007) report that due to the presence of certain lipids in structure, bark is able to act as a passive accumulator of organic compounds in the air over the life of the tree [73]. Nevertheless, according to Zhou et al. (2014, 2015), tree bark should be used as an indicator of atmospheric organic contaminants only in some situations because, considering pollution by organic substances, bark is not suitable for determining precise changes in the atmosphere [77-78]. Studies of Wang et al. (2015) carried out over four seasons of the year confirm that tree bark can be an indicator of short-chain chlorinated paraffins, another group of POPs (SCCPs) [58]. The exact qualitative and quantitative analysis of PCBs, carried out on samples of bark from the area of the former production site in Sauget, Illinois (USA), confirmed the high correlation between proximity to the place of PCB emissions and the content in the bark of trees persisting even after several years of cessation of emissions [79, 82]. Thus, tree bark is able to reveal the actual state of air pollution and topsoil by organic substances.

There is no doubt that the analysis for the content of organic compounds of atmospheric origin is currently the main direction of research on the bark of trees as a bioindicator. The usefulness of tree bark for determining atmospheric POPs distribution has been proven experimentally, e.g., in extensive research in China [50, 58, 72, 77-78],

Table 1. Alphabetic list of selected tree species whose bark has been used in studies of air quality along with chronologically arranged references.

Genus:	Species:	Determined parameters:	Location:	Reference:
Acacia	*Acacia karroo*	Cr(VI)	Northwest South Africa	Mandiwana K.L. et al., 2006 [59]
Acer	*Acer platanoides*	pH (SO$_2$)*, buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		pH (SO$_2$), Ca, K, Na	Frankfurt am Main, Hesse (Germany)	Lötschert W. and Köhm H.J. 1977 [46]
	Acer pseudoplatanus	pH (SO$_2$), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		$^{355}U/^{238}U$ ratio	North Wales, northeast Derbyshire, Scilly Isles, Drax in Yorkshire (UK)	Bellis D.J. et al., 2001 [38]
		Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Ti, V, Zn	Sheffield (United Kingdom)	Schelle E. et al., 2008 [8]
		pH (SO$_2$)	Cities of Upper Silesian Industrial Region (Poland)	Steindor K. et al., 2010 [45]
Aesculus	*Aesculus hippocastanum*	pH (SO$_2$), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		Cd, Cu, Pb, Zn	Edirne, Edirne Province (Turkey)	Yilmaz R. et al., 2006 [48]
Alnus	*Alnus glutinosa*	pH (SO$_2$), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
	Alnus incana		Białowieża National Park, Niepołomice Forest (Poland)	Grodzińska K. 1977 [29]
Betula	*Betula pendula*	pH (SO$_2$), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		Ba, Ca, Cd, Cu, Fe, K, Mn, Ni, P, Pb, Rb, S, Sr, Zn	Southwest Finland	Saarela K.E. et al., 2005 [68]
	Betula pubescens	pH (SO$_2$), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
Caesalpinia	*Caesalpinia pluviosa*	Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Mn, Na, P, Rb, S, Sr, Zn	São Paulo (Brasil)	Moreira T.C.L. et al., 2016 [60]
Carpinus	*Carpinus betulus*	pH (SO$_2$), buffer capacity	Białowieża National Park, Niepołomice Forest (Poland)	Grodzińska K. 1977 [29]
Cassia	*Cassia fistula*	Cr, Cu, Fe, Pb, Zn	Chiang Mai (Thailand)	Janta R. et al., 2016 [37]
Cedrus	*Cedrus deodara*	PCDD/Fs, PBDEs, PCBs	Luqiao (China)	Wen S. et al., 2009 [50]
Cinnamomum	*Cinnamomum camphora*	PAHs	Southern Jiangsu, (China)	Zhou L. et al., 2014 [77]
		PCBs, PBDEs		Zhou L. et al., 2015 [78]
Coryllus	*Coryllus avellana*	pH (SO$_2$), buffer capacity	Białowieża National Park, Niepołomice Forest, (Poland)	Grodzińska K. 1977 [29]
Cupressus	*Cupressus semervirens*	pH (SO$_2$); Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Zn	Amman (Jordan)	El-Hasan T. et al., 2002 [19]
Fagus	*Fagus sylvatica*	pH (SO$_2$), electrolytic conductivity	Navarra (Spain)	Santamaria J.M. and Martin A. 1997 [31]
		$^{35}U/^{238}U$ ratio	North Wales, northeast Derbyshire, Scilly Isles, Drax in Yorkshire (United Kingdom)	Bellis D.J. et al., 2001 [38]
		As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, V, Zn; PCBs, PCDD/Fs	Strasburg (France) Kehl (Germany)	Guéguen F. et al., 2011 [12]
	Fagus longipetiolata	PAHs	Southeast China	Wang et al., 2004 [72]

Table 1. Continued.

Fraxinus	*Fraxinus excelsior*	pH (SO_2), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
			Białowieża National Park, Niepołomice Forest, (Poland)	Grodzińska K. 1977 [29]
		pH (SO_2), Cd, Mn, Ni, Pb	Frankfurt am Main, Hesse (Germany)	Lötschert W. and Köhm H.J. 1977 [46]
		Al, As, Ba, Ca, Ce, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hf, K, La, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Si, Sm, Sn, Sr, Ti, U, V, W, Zn, Zr	Grenoble (France)	Catinon M. et al., 2009 [33]
		pH (SO_2)	Cities of Upper Silesian Industrial Region (Poland)	Steindor K. et al., 2010 [45]
		Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Ni, U, Pb, Rb, Sb, Se, Si, Th, Ti, U, V, Zn	Saint-Martin-d'Hères (France)	Catinon M. et al., 2012 [34]
Moringa	*Moringa oleifera*	As, Ca, Co, Cr, Cu, Cd, Fe, K, Mg , Mn, Ni, Pb, Zn	Agra, Aligarh (India)	Gupta J. et al., 2014 [56]
Olea	*Olea europaea*	46 elements including: Al, As, Cl, Cu, Fe, La, Mn, Na, Sc, Ti	Northwest Portugal	Pacheco A.M.G et al., 2001, 2002 [65, 66].
Parkia	*Parkia biglobosa*	Cd, Cr, Cu, Mn, Ni, Pb, Zn	North-central Nigeria	Olatunji O.S. et al., 2016 [13]
Picea	*Picea* sp.	pH (SO_2), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
	Picea abies	Ba, Ca, Cd, Cu, Fe, K, Mn, Ni, P, Pb, Rb, S, Sr, Zn	Southwest Finland	Saarela K.E. et al., 2005 [68]
		^{137}Cs	Northwest, southwest, and central Romania	Cosma C. et al., 2016 [70]
Pinus	*Pinus* sp.	pH (SO_2), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		SCCPs	Beijing (China)	Wang T. et al., 2015 [58]
	Pinus brutia	PAHs	Iskenderun, Hatay Province (Turkey)	Falay E.O. et al., 2013 [76]
		48 elements including lanthanides (La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb)	Aliağa, Izmir Province (Turkey)	Odabasi M. et al., 2016 [11]
	Pinus sylvestris	pH (SO_2), buffer capacity	Białowieża National Park, Niepołomice Forest, (Poland)	Grodzińska K. 1977, 1979 [29, 30]
		pH (SO_2) electrolytic conductivity; Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, Zn	Northern Finland, Kola Peninsula (Russia)	Poikolainen J. 1997 [44]
		pH (SO_2), electrolytic conductivity	Navarra (Spain)	Santamaria J.M. and Martin A. 1997 [31]
		Al, As, B, Ca, Cd, Ce, Cr, Cu, Fe, Hg, La, Mo, Nd, Ni, Pb, Sr, Ti, V, W, Zr, Zn; NH_4^+, NO_3^+, PO_4^{+3}, SO_4^{+2}; PAHs, a-hexachlorocyclohexane (a-HCH) and dichlorodiphenyltrichloro-ethane (DDT)	Throughout Germany, also areas in Denmark, Norway, Poland, Russia	Schulz Z. et al., 2000 [63, 64]
		^{35}U/^{238}U ratio.	North Wales, northeast Derbyshire, Scilly Isles, Drax in Yorkshire (UK)	Bellis D.J. et al., 2001 [38]
		Cd, Cu, Hg, Pb, S, Zn; PAHs, phenols	Świętokrzyskie Mountains (Poland)	Migaszewski Z. et al., 2002 [25]
		Ba, Ca, Cd, Cu, Fe, K, Mn, Ni, P, Pb, Rb, S, Sr, Zn	Southwest Finland	Saarela K.E. et al., 2005 [68]

Table 1. Continued.

Pinus	*Pinus sylvestris*	Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Stalowa Wola (Poland)	Samecka-Cymerman A. et al., 2006 [26]
		$^{206}Pb/^{207}Pb$ ratio	Throughout Scotland (United Kingdom)	Patrick G.J. and Farmer J.G., 2007 [69]
		PAHs	Palermo area (Sicily, Italy)	Orecchio S. et al., 2008 [74].
		pH (SO_2); Cd, Cu, Pb, Zn	Niepołomice Forest (Poland)	Chrzan A., 2015 [32]
		pH (SO_2); Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn	Rîga (Latvia)	Čekstere G. et al., 2015 [57]
	Pinus massoniana	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Qujiang, Dinghushan (China)	Kuang Y.W. et al., 2007 [2]
	Pinus nigra	pH (SO_2), electrolytic conductivity	Navarra (Spain)	Santamaria J.M. and Martin A., 1997 [31]
		Cr, Cu, Fe, Pb	Salzburg (Austria), Belgrade (Serbia), Thessaloniki (Greece)	Sawidis T. et al., 2011 [4]
		Hg	Mt. Amiata, Toscany (Italy)	Chiarantini L. et al., 2016 [41]
	Pinus pinaster	pH (SO_2); Ca, Cd, Cu, K, Mg, Na, Ni, Pb, Zn	Madrid (Spain)	Cutillas-Barreiro L. et al., 2014 [55]
	Pinus pinea	PAHs	Iskenderun, Hatay Province (Turkey)	Falay E.O. et al., 2013 [76]
		48 elements including lanthanides (La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb)	Aliağa, Izmir Province (Turkey)	Odabasi M. et al., 2016 [11]
	Pinus resinosa	PAHs, alkylated-PAHs, nitro and oxy-PAHs, PBDEs and novel brominated flame retardants (novel BFRs)	Toronto, Ontario (Canada)	Rauert C. and Harner T., 2016 [81]
Platanus	*Platanus hybrida*	Al, As, Ba, Ce, Co, Cr, Cs, Cu, Fe, Hf, Hg, K, Mg, Mn, Rb, Sb, Sc, Se, Sm, Ta, Th, Ti, U, V, Zn	Northern Portugal	Pacheco A.M.G et al., 2008 [67]
	Platanus orientalis	Cr, Cu, Fe, Pb	Salzburg (Austria), Belgrade (Serbia), Thessaloniki (Greece)	Sawidis T. et al., 2011 [4]
Populus	*Populus* sp.	pH (SO_2), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		pH (SO_2); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}	Throughout the Netherlands	Wolterbeek H. Th. et al., 1996 [62]
	Populus x canadensis	pH (SO_2); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}		Van Dobben H.F. et al., 2001 [24]
	Populus nigra	As, Au, Ce, Co, Cr, Cu, La, Mn, Mo, Ni, Sb, Sm, Ti, Th, U, V, W	Kiev (Ukraine)	Berlizov A.N. et al., 2007 [39]
		Cd, Cu, Ni, Pb, Zn	Navodari (Romania)	Barbeş L. et al., 2014 [54]
	Populus tremula	Cd, Cu, Hg, Pb, S, Zn; PAHs, phenols	Świętokrzyskie Mountains (Poland)	Migaszewski Z. et al., 2002 [25]
Prunus	*Prunus serrula*	Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Ti, V, Zn	Sheffield (United Kingdom)	Schelle E. et al., 2008 [8]

Table 1. Continued.

Quercus	*Quercus* sp.	pH (SO_2); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}	throughout Netherlands	Wolterbeek H. Th. et al., 1996 [62]
	Quercus crispula	As	Ashio, Tochigi prefecture (Japan)	Bellis D.J. et al., 2003 [61]
	Quercus faginea	pH (SO_2), electrolytic conductivity	Navarra (Spain)	Santamaria J.M. and Martin A. 1997 [31]
	Quercus ilex	pH (SO_2), electrolytic conductivity	Navarra (Spain)	Santamaria J.M. and Martin A. 1997 [31]
		As, Cd, Co, Cu, Fe, Mn, Ni, Pb, V, Zn	Genova, Liguria (Italy)	Drava G. et al., 2016 [9]
		As, Cd, Co, Cu, Fe, Mn, Ni, Pb, V, Zn	Genova, Rapallo, Liguria (Italy)	Minganti V. et al., 2016 [35]
	Quercus petraea	Al, As, Ce, Co, Cr, Cs, Fe, Hf, Hg, La, Mn, Na, Ni, Rb, S, Sb, Sc, Se, Th, Ti, U, V, W, Zn	Throughout the Czech Republic	Böhm P. et al., 1998 [1]
	Quercus pubescens	As, Cd, Co,Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Sn, Zn; ^{15}N, ^{18}O, ^{13}C; PCDDs, PCDFs	Venafro Plain, Molise (Italy)	Cocozza C. et al., 2016 [28]
	Quercus robur	pH (SO_2), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
			Białowieża National Park, Niepołomice Forest (Poland)	Grodzińska K. 1977, 1979 [29, 30]
			Navarra (Spain)	Santamaria J.M. and Martin A. 1997 [31]
		Al, As, Ce, Co, Cr, Cs, Fe, Hf, Hg, La, Mn, Na, Ni, Rb, S, Sb, Sc, Se, Th, Ti, U, V, W, Zn	Western Czech Republic	Böhm P. et al., 1998 [1]
		pH (SO_2); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}	Throughout the Netherlands	Van Dobben H.F. et al., 2001 [24]
		Cd, Cu, Hg, Pb, S, Zn; PAHs, phenols	Świętokrzyskie Mountains (Poland)	Migaszewski Z. et al., 2002 [25]
		Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Ti, V, Zn	Sheffield (United Kingdom)	Schelle E. et al., 2008 [7]
		^{137}Cs	Northwest, southwest, and central Romania	Cosma C. et al., 2016 [70]
Robinia	*Robinia pseudoacaccia.*	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Oleśnica, Lower Silesia Province (Poland)	Samecka-Cymerman A. et al., 2009 [3]
		pH (SO_2)	cities of Upper Silesian Industrial Region (Poland)	Steindor K. et al., 2010 [45]
Salix	*Salix* sp.	pH (SO_2), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		pH (SO_2); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}	Throughout the Netherlands	Wolterbeek H. Th. et al., 1996 [62]
	Salix alba	pH (SO_2); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}	Throughout the Netherlands	Van Dobben H.F. et al., 2001 [24]

Table 1. Continued.

Taxus	*Taxus baccata*	pH (SO₂)	Cities of the Upper Silesian Industrial Region (Poland)	Steindor K. et al., 2010 [45]
		Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, N, Ni, P, Pb, Zn	Wrocław, Lower Silesia Province (Poland)	Samecka-Cymerman A. et al., 2011 [51]
Terminalia	*Terminalia catappa*	Cu, Fe, Mn, Ni, Pb, Zn	Ogbomoso (Nigeria)	Olajire A.A. and Ayodele E.T. 2003 [49].
		Ba, Al, Fe, K, Sr, Zn	Paranaguá Paraná state (Brazil)	Gurgatz M. et al., 2016 [10]
Tilia	*Tilia* sp.	pH (SO₂), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, V, Zn; PCBs, PCDD/Fs	Strasburg (France) Kehl (Germany)	Guéguen F. et al., 2011 [12]
		Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, Sb, Si, Sm, Sn, Sr, Tb, Th, Ti, Tm, U, V, Y, Yb, Zn, Zr; $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{207}Pb$ ratios		Guéguen F. et al., 2012, 2012 [62, 63]
		Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	Banja Luka (Bosnia and Herzegovina)	Škarbić B. et al., 2012 [40]
	Tilia cordata	pH (SO₂), Ca, K, Na	Frankfurt am Main, Hesse (Germany)	Lötschert W. and Köhm H.J. 1977 [46]
		pH (SO₂), buffer capacity	Białowieża National Park, Niepołomice Forest (Poland)	Grodzińska K. 1977, 1979 [29, 30]
	Tilia platyphyllos	pH (SO₂), Ca, K, Na	Frankfurt (Germany)	Lötschert W. and Köhm H.J. 1977 [46]
Tipuana	*Tipuana tipu*	Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Mn, Na, P, Rb, S, Sr, Zn	São Paulo (Brazil)	Moreira T.C.L. et al., 2016 [60]
Ulmus	*Ulmus* sp.	pH (SO₂), buffer capacity	Stockholm (Sweden)	Skye E. 1968 [21]
		pH (SO₂); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}	Throughout the Netherlands	Wolterbeek H. Th. et al., 1996 [62]
	Ulmus x hollandica	pH (SO₂); As, Br, Ca, Cd, Ce, Co, Cr, Cs, Fe, Hg, K, La, Na, Ni, Sb, Sc, Se, Sm, Th, Zn; NH_4^+, NO_3^+, SO_4^{+2}	Throughout the Netherlands	Van Dobben H.F. et al., 2001 [24]
	Ulmus rubra	U	southwest Ohio (USA)	Conte E.R. et al., 2016 [14]

*pH (SO₂) - bark acidity test for the sulphur contained.

wherein many of these compounds are deliberately introduced into the environment as cheap and efficient pesticides [80]. Determining organohalogen compounds (OHCs) like organochlorine pesticides (OCPs), dechlorane plus (DP), and novel brominated flame retardants (NBFRs) in tree bark has recently been described by Chinese researchers. Material examined from rapidly growing city of Kaiyuan in Yunnan Province [83] and the Yellow River region [85] showed substantial contamination of these compounds in China and promising properties of the bark as a sensitive marker of this ubiquitous organic compound in the environment.

Examples of Air Quality Determination Using the Bark Deriving from Various Species of Trees

Tree bark is in large part a dead organ. Therefore, it is treated by most authors as a passive indicator of air pollution. It might appear as if the bark of most tree species can act as an air pollution bioindicator which, however, turns out not to be true [2, 20]. Bark is an organ with its own unique chemical characteristics, such as distinctive acidity depending on the species [21, 29-32, 42, 44]. It is well known that the pH value influences the absorption

of elements from soil, and, therefore, bark acidity might interfere with the efficient adsorption of impurities, e.g., heavy metals [33-34]. Therefore, for effective air monitoring a species of known biology should be selected and, where possible, with stable chemical conditions. Table 1 shows selected scientific reports showing the potential use of bark of various trees in the identification of air pollution over the last half century.

Studies of air quality using tree bark both in Poland and in other European countries are especially often conducted using the bark of trees from the genus *Pinus*, including Scots pine (*Pinus sylvestris*) [25, 29-32, 38, 44, 57, 63-64, 68-69], the needles of which are a well documented bioindicator of air pollution. As a species common to nearly all of north-central Europe, *P. sylvestris* is a valuable source of information on the spread of atmospheric pollutants, both organic and inorganic. The usefulness of pine bark is, beyond its high porosity, based on a complete lack of metabolic processes in the dead part, where processes of dust accumulation may occur. As a result, Scots pine bark almost perfectly reflects the level of contamination of organic and inorganic substances [63-64]. Despite the fact that the Scots pine is a species tolerant to soil type and pH, it prefers acidic soils, which may affect the results. Furthermore, the pine is a coniferous species, which sometimes cannot fully represent the area. Among deciduous species, bark samples from the oak *Quercus* sp., mostly *Q. robur* [1, 7, 21, 24-25, 29-31, 70], or linden (*Tilia* sp.) [12, 21, 29-30, 40, 46, 63] are used equally often to study air quality. Bioindication of air quality in Europe is also often based on the analysis of the bark of the ash, beech, or poplar [12, 21, 24-25, 29-31, 33-34, 38-39, 45, 46, 62]. In northern Europe, trees of the genus *Betula* are especially popular species whose bark is used to determine air quality [21, 69]. On the other hand, in the southern part of Europe, the common olive tree is a popular species for testing air quality [65-66].

Conclusions

Tree bark is a valuable source of information about pollutants in the environment which is confirmed by scientific reports. The use of tree bark in assessing air quality is particularly useful because of:
1. Absorbent properties of the bark, enabling determination of permanent and temporary air pollution of different chemical origins
2. The ability to compare data with the selection of common species in the studied areas and the ability to map the spread of contamination and identify emitters and pollutants
3. Observation of the effect of pollution on the condition of the material (ecotoxicology)
4. Wide availability of the material, ease, and low costs of sampling

Despite the fact that elemental analysis remains the dominant direction of environmental research based on tree bark, far-reaching progress has been made over the last 50 years on approaches to the use of the plant material in monitoring air quality. The most commonly performed physical and chemical tests of air quality relate only to determine the temporary content of impurities in the air. There is no doubt that the inclusion of bioindicative research, including the use of tree bark in standard physicochemical air monitoring would enable holistic analysis of air quality. Such monitoring could provide information on both temporary and periodic air pollution as well as valuable ecotoxicological information.

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