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### 26 Passive Monitoring of Airborne Pollutants, Particularly Trace Metals, with Tree Bark

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### **26.1 Introduction**

In this chapter a summary of general possibilities and problems of the use of tree bark as a bioindicator of air pollution is presented. After a brief account on air pollution monitoring by determination of bark pH levels and of general environmental pollution by the measurement of conductivity of bark extracts, attention is focused mainly on the use of tree bark as a bioindicator of trace elements. Furthermore, an evaluation of basic principles and problems of the method is attempted.

Previous reviews of this subject have been published by Martin and Coughtrey (1982) and Arndt et al. (1987).

## 26.1.1 Basic Principles and Aims of Air Pollution Biomonitoring with Tree Bark

The bark of a tree is produced by the activity of the cork cambium, and mainly consists of cork. According to the Committee on Nomenclature of the International Association of Wood Anatomists (1933), it can be defined as all tissues of the tree, outside the cambium layer. In older trees it is divided into inner (living) and outer (dead) bark.

Bark protects the tree against harmful mechanical, chemical and biological influences, as well as excessive evaporation. While the tree trunk continues to grow and increases its diameter, the outermost parts of the bark are shed. Vaucher (1990) characterizes eighteen different varieties of bark, and points out that each tree has its typical bark, as each finger its print. Similar kinds of bark exist, but there are no identical ones. Bark of many tree species is exposed to the atmosphere for a considerable period of time, its duration depending on the species.

The basic assumption in using bark for biomonitoring purposes is, that levels of pollutants in bark should reflect the levels of environmental pollution.

The bulk of substances is assumed to accumulate on the surface and in the outermost dead bark cells (Fig. 1). In this tissue no substantial active or passive translocation of investigated elements into the wood should take place. If such processes occur, they should be quantified and accounted for in a careful interpretation of analytical results.

Besides radial movements also an axial transport of substances from roots or assimilation organs into the bark may influence its composition. The extent of this shift may vary for each investigated element, depending on its mobility.





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The developing of the method began with the basic article of Stäxang (1969) (compare also Skye 1968), who took samples in the following way: Thin chips of the outermost parts of the bark were cut or scraped off from the surface with a knife after cleaning the area of epiphytic organisms with a strong brush in a height ranging from 1.0 to 1.5 meters above ground. According to Grodzinska (1982), sample width should range between 2 and 3 mm and the direction, where sampling is done, should always be the same.

Different authors took samples from different heights of the stem (see Section 26.3.3), though it turned out to be useful to collect bark samples at breast-height, as done, e.g., by Karandinos et al. (1985).

In the true sense of the word, analyzing bark is no "bio"-monitoring, because only a dead tissue is sampled. However, as the samples are obtained from a living organism, the tree, we do agree with Härtel (1982), who also justified this term for the above mentioned reason.

The principles, described above, deal with the general range of levels of airborne particle input, accumulated over a long, though not exactly defined period of time. In this concern biomonitoring is done on a regional scale.

A different way of using the material for biomonitoring is the time dependent analysis by the technique of proton induced x-ray emission (PIXE). This method is based on the fact, that bark of several species, e.g. Scots pine (*Pinus sylvestris*), is formed in seperate consecutive layers. The cross section of the bark appears, thus, stratified. Analysis of such layers may give information about the extent of pollution in a specified period, respectively certain years.

Time series have been studied in order to get information about possible variations in element levels and composition resulting from changes of levels of airborne substances in the environment. Investigations, in which this method has been used are, e.g., Raunemaa et al. (1982, 1983, 1987a, b) and Lövestam et al. (1990).

# 26.1.2 History of the Use of Tree Bark as a Medium of Bioindication - a Survey

The first investigation of air pollution monitoring with tree bark appears to have been performed in southern Sweden by Stäxang (1969). She collected bark samples

of Acer platanoides, Fraxinus excelsior, Alnus glutinosa, Betula verrucosa, Populus tremula, Quercus robur, Ulmus glabra and Tilia cordata and determined pH levels of bark extracts and other parameters. The results were examined with respect to an apparent acidification of the material reflecting the recent acidification of the environment. The pH of bark samples of all species tended to be lower in urban areas, which may indicate the suitability of the applied technique.

Another step in the development of this method were the investigations of Härtel and Grill (1972), who introduced an estimation of conductivity of bark extracts as a measure of general air pollution. Furthermore, a photometric determination of levels of sulfur in the material was used to indicate sulfur dioxide pollution.

In general, results of both methods were in good agreement with the sulfur and non sulfur pollution of the air and the distance to emission sources.

Many researchers in this field followed the lines proposed in the basic studies on determination of bark pH and sulfur content as well as conductivity, i.e., Grodzinska (1971, 1977, 1978a, b, 1979, 1982), Lötschert (1971, 1977a, b), Härtel and Grill (1972a, b), Lötschert (1972), Hutter (1973), Johnsen and Søchting (1973), Lötschert and Köhm (1973a, b, 1977a, b, 1978, 1979), O'Hare (1974), Köhm (1976a, b), Zdanowska (1976), Härtel (1977, 1980, 1982, 1987), Kienzl (1978), Grill and Hofer (1979), Härtel et al. (1980).

The majority of investigators used deciduous tree species, because (a) the natural variability of pH values seems to be lower and (b) pH levels of the bark are higher in those trees, which makes them more sensitive to acid pollution.

Barkman (1958) stated, that bark of deciduous trees, being less acid under unpolluted conditions, is a more sensitive bioindicator of air pollution, than bark of coniferous trees.

Kienzl and Härtel (1979a) and Härtel (1982) pointed out, that coniferous trees did not proof to be sensitive bioindicators of sulfur pollution by using the method of measuring bark pH levels.

In addition, Kreiner (1986) found fundamental differences in the reaction of bark of *Aesculus hippocastanum* and *Picea abies* with respect to pH levels of bark reflecting the content of sulfur in the air. He reported, that pH levels of coniferous trees grown under unpolluted conditions are more acid than those of deciduous species.

Similar results were given by Mathis and Tomlinson (1972), Johnsen and Søchting (1973), Swieboda and Kalemba (1979), and Kreiner (1984). To demonstrate the sensitivity of tree bark as an indicator of acid pollutions, relations between sulfur contents of bark and of needles of coniferous tress were evaluated by Härtel and Grill (1972). They found high levels of correlations between the two parameters. Köhm (1976) compared sulfur contents of bark with those of the atmosphere and found good correlations, the levels depending on the tree species.

#### 26.2 Trace Metals in Tree Bark

The input of elements, among them heavy metals, into ecosystems due to human activity has become an increasing burden during the last centuries. Trace elements, even if deposited constantly in small rates over long periods of time, accumulate in the environment and will probably pose an increasing hazard in the future.

Thus, it seems important to develop and improve a passive long term monitoring technique for trace metals in order to assess the kind and degree of pollution of ecosystems.

Investigations of several groups in this field started mainly with sampling of bark of deciduous trees, as outlined in Section 26.1.2 (Grodzinska 1971; Lötschert and Köhm 1973a; Köhm 1976).

This may result from the fact, that in early investigations bark of such trees was used for monitoring of acidic air pollution.

Later on, also coniferous trees were used, for example by Härtel and Grill (1972) and Härtel (1982). Apparently, in recent years there seems to be a growing number of researchers beginning to analyze bark of coniferous trees as indicators of heavy metals, e.g., Gustke (1991) in Germany, or Herman (1991) in Austria.

The estimation of conductivity of bark extracts is a well known way of monitoring air pollution (Section 26.1.2). However, a disadvantage of this method is its inability to distinguish between different elements. If more specific information about the kind of pollutants is required, analytical methods have to be employed. e.g., instrumental neutron activation analysis (INAA), atomic absorption spectrometry (AAS) or proton induced x-ray emission (PIXE).

Distributions of Pb and Cd were often investigated, probably because of their toxicity and ubiquitous occurrence in polluted ecosystems.

According to Lötschert and Köhm (1978), Pb can be used as an indicator of pollution by automobile exhaust fumes, whereas Cd may be taken as a rough measure of the general anthropogenic pollution of the environment. This assumption may be true in urban areas, like Frankfurt/M., Germany, where the investigation took place. However, this is a too far reaching generalization, since in many places particular elements other than Cd are polluting the environment.

## **26.2.1** Investigations Dealing with Levels of Trace Elements in Tree Bark — a Selection of General Studies

Studies reporting levels of trace elements in tree bark from sites considered more or less unpolluted are an important source of reference. Such data constitute a base line for an assessment of element levels observed in polluted locations. In industrialized regions, such as Central Europe, places that are not affected by environmental pollution are, however, difficult to find. Several large-scale research projects are conducted in Germany, in which element levels and fluxes in forest e r

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ecosystems are under investigation. Among them are the "Solling Project" in the northern region and investigations being performed at the "Bärhalde" in the Black Forest, south-west Germany. Results have been published in numerous reports, e.g., Ellenberg (1971, 1973), Pavlov (1972), Mayer and Heinrichs (1981), Mayer (1981), Matzner et al. (1982), Raisch (1983), Raisch and Zöttl (1983), Ellenberg et al. (1986). For other regions compare Grodzinski and Yorks (1981).

In Tab. 1 levels of several elements in tree bark of beech and spruce forests are presented in order to give information about background levels of contents of elements in bark in the "Solling" and the "Bärhalde".

In eastern Poland research was conducted on a large scale in the "Niepolomice" forest. Results of this project are published, e.g., by Grodzinska (1980).

**Tab. 1.** Contents of Major and Trace Elements in Bark of Spruce and Beech Trees in the "Solling", Northern Germany and the "Bärhalde", South Western Germany

The biological function of the elements is indicated as (+) for essential nutrients. (?) for possible nutrients in certain plant groups, and (\*) for toxic elements (data from Raisch 1983, and Ellenberg et al. 1986)

Element	Character	Spruce	Solling Beech	Bärhalde Spruce
Major Elem	ents g (kg dry wt.	) <sup>-1</sup>		
Na	?	0.03	0.03	0.028 - 0.052
K	+	3.1	1.9	2.25 - 5.25
Mg	+	0.7	1.07	0.52 - 0.92
Са	+	8.7	6.2	5.6 - 8.6
Trace Eleme	ents mg (kg dry w	$(t.)^{-1}$		
ln	+	1.1	0.91	0.38 - 0.82
<b>~</b> Ċr	*	14.0	12.0	0.51 - 1.23
Со	?	0.6	0.7	0.06 - 0.24
Ni	?	15.0	11.0	1.2 - 5.0
A1	*	70.0	50.0	105.0 - 150.0
Cu	+	32.0	32.0	4.46 - 9.26
Zn	+	178.0	41.0	118.0 - 222.0
Cd	*	1.4	0.06	0.3 - 1.6
Pb	*	19.0	35.0	1.5 – 2.8

#### 26.2.2 Concentrations of Trace Metals in Bark of Trees along Roads — Pb as an Indicator of Automobile Exhaust Fumes

Despite a growing trend in several industrialized countries to use unleaded petrol, automobile exhaust fumes are still a major source of Pb emissions. Alkyl-lead compounds, mainly tetraethyl- and tetramethyl-lead, are added to petrol as anti-knocking agents. In Germany the levels ranged up to  $0.6 \text{ g} \cdot \text{L}^{-1}$ , or higher until 1972.

A considerable part of the Pb is released into the environment after burning of the petrol in the engine, especially in the form of PbClBr,  $\alpha$ -,  $\beta$ -NH<sub>4</sub>Cl · 2 PbClBr, 2 NH<sub>4</sub>Cl · Br, and 3 Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (Hirschler and Gilbert 1964).

A number of researchers examined Pb concentrations in bark of trees along roads, in order to get information of pollution levels by automobile exhausts (Ault et al. 1970; Daines et al. 1970; Heichel and Hankin 1970; Holtzman 1970; Smith 1971; Fergusson et al. 1980).

Concentrations of Pb in bark of several tree species near a road in New Zealand were measured by Ward et al. (1974) with atomic absorption spectrometry. The tree species included *Acer pseudoplatanus, Aesculus hippocastanum, Fraxinus excelsior, Quercus robur, Platanus orientalis* and *Ulmus procera*. Significantly higher concentrations of Pb in bark were observed in trees near the road as compared to those of background sites. Bark samples facing the roadway showed higher levels than those of the opposite side. Furthermore, Pb concentration from the side of the tree that was exposed to the prevailing wind direction was higher than on the other sides.

Hampp and Höll (1974) reported various levels of Pb in bark of *Robinia* pseudoacacia, Tilia cordata and Acer platanoides depending on traffic density along streets in the city of Munich, Germany. They also observed a height-dependent Pb distribution (Fig. 1) and found highest levels at about 150 cm above ground. After washing bark samples in distilled water for ten minutes, only about 40% of the initial Pb concentration was found. This indicates, that the major part of Pb was deposited superficially. They also analyzed bark samples from various depths under the surface of the trunk and found highest concentrations of Pb in the outermost two millimeters (Fig. 2).

Baes and Ragsdale (1981) analyzed Pb levels in bark samples of various tr species in Atlanta, USA. They found higher concentrations on the side of the trunk



**Fig. 2.** Lead concentrations at various depths in bark of *Robinia pseudoacacia*, growing in the city of Munich, Germany (after Hampp and Höll 1974).

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facing the road, than on the opposite side. Such differences on the comparatively small perimeter of a tree trunk indicate the sensitivity of the monitoring technique.

Szopa et al. (1973) found higher concentrations of Pb in bark of black oak (Quercus nigra) and shortleaf pine (Pinus echinata) trees near a roadway in Missouri, USA, than in samples of trees in some distance from the road. They reported elevated Pb contents in bark of the lower parts of the trunk. This may be a result of an increased Pb pollution at the ground level. Accordingly, the position of the emission sources (distance and height above ground) may be an important factor influencing the distribution of an element in tree bark.

A correlation between the distance of the sampled tree bark to a road in Finland and the observed levels of Pb was described by Laaksovirta et al. (1976).

### **26.2.3** Monitoring of Air Pollution in Urban and Industrialized Areas

Besides the studies conducted with trees alongside roadways, there is a considerable number of investigations using tree bark analysis to monitor trace element pollution in densely populated areas.

Lead, Cd, and other trace metals are found in substantial quantities in emissions of various industrial processes as well as in dust particles originated by burning of fossile fuels in power plants or private households. Hence, in urban areas it seems useful to measure concentrations of these trace metals in bark in order to monitor mount and composition of anthropogenic emissions.

<sup>7</sup> Results of investigations conducted by Kosmus and Grill (1986) in the city of Graz, Austria, demonstrated the usefulness of bark analyses of spruce as indicators of different kinds of pollution.

Lötschert and Köhm (1978, 1979) determined the distributions of several metals (Pb, Cd, Ni, Mn) in bark of *Fraxinus excelsior* trees in the city of Frankfurt/M., Germany, in order to test the suitability of the method for monitoring airborne pollutants. They were able to draw maps with isolines of equal concentrations of Pb and Cd, depending on local emission sources, such as main traffic roads, centers of heating power of private households, as well as industrial emitters and prevailing wind direction. This was not possible in the case of Mn which is more mobile in bark. The authors proposed, that it could be washed off from bark by rain with high concentrations of sulfuric acid, and might also be partly taken up from the soil.

In contrast, Raisch and Zöttl (1983), who analyzed various compartments of *Picea abies* trees, reported no adsorption of Cd on vegetation surfaces. The contents of this metal in plant tissues only reflect the extent of uptake via the roots.

In northern Sweden Symeonides (1979) observed considerably increased concentrations of Pb, Cd, Zn and Cu in bark samples of *Pinus sylvestris* (compare also Smith 1973) collected near a smelter complex, as compared to those from unpolluted sites. He described metal specific differences. In a comparison of polluted and unpolluted sites largest differences were observed for Pb, followed by Cu, Cd and Zn.

Little (1974) reported high accumulations of Pb, Cd and Zn in bark of elm (*Ulmus procera*) trees near a zinc-lead smelting complex near Bristol, UK. The levels depended on distance and prevailing wind direction.

Trüby and Zöttl (1990) reported the contents of Pb, Cd and Zn in bark and other tissues of spruce (*Picea abies*) in the highly polluted area of Stolberg (Eife Germany). Concentrations of Pb and Cd in trees near a large Pb processing industrial complex were significantly higher than in spruce from sites farther away from the emission source. Contents of Zn, however, did not show significant differences between the two locations. In addition, they described effects of different lime contents of the soil, resulting in different contents and distributions of heavy metals in bark. The reasons may be variations in the bark formed under different circumstances.

Hall et al. (1975) compared levels of Pb, Cu and Zn of bark from various polluted and unpolluted sites presented by several authors. Concentrations of the metals were always higher in polluted areas. Even though the sites may not have been fully comparable, the results indicate a relation between environmental pollution and the levels of pollutants in tree bark.

The same elements were investigated by Barnes et al. (1976) in bark of Norway spruce (*Picea abies*) and white beam (*Sorbus aria*) from three sites in Scotland, UK. The authors chose a relatively unpolluted forest site, a location in the center of Glasgow, and a site close to a roadway in some distance from Glasgow. For Pb in bark they reported a correlation with traffic density, in agreement with the reports mentioned in Section 26.2.2. In addition, a similar, though somewhat weaker correlation was found for Zn and Cu. They also focused attention on differer tree species with different bark types, and denied an influence of those on concentrations of elements in bark in polluted areas.

In contrast, Young and Guinn (1966), who analyzed bark samples of several tree species for twelve elements, reported significant differences of the analyzed element contents between the species (and by that, different bark types), ranging up to a factor of eight.

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Some interesting results, demonstrating the general suitability of bark for biomonitoring of airborne pollutants are presented by Trüby (1988). He compared the contents of Pb in various tissues of *Pseudotsuga menziesii*, *Abies alba* and *Quercus robur* growing at three different sites: on ore mine spoils, close to a highway and on comparatively unpolluted brown earth soil. Pb contents of the inner bark of trees from the unpolluted brown earth soil were comparatively smaller than those of the geogenically polluted sites. In the outer bark, however, differences were much lower. The Pb levels in bark of trees from ore mine spoils were only slightly elevated. In contrast, Pb concentrations in bark of roadside trees were about ten times higher in comparison. From his results Trüby (1988) concluded that only small quantities of Pb were transported from the roots into the outer bark of the stem. Furthermore, he found no indication for Pb uptake by assimilation organs, and supposed, that the major part of Pb found in the outer bark is of atmospheric origin. This observation is crucial for an application of bark for biomonitoring air pollution. Also Trüby and Zöttl (1988) focused on Pb, Cd and Zn in bark of *Abies alba* and *Pseudotsuga menziesii* on a geogenically highly polluted and a relatively unpolluted site in the Bärhalde, southwest Germany. They pointed out, that nearly all the Pb in bark originated from atmospheric pollution and was accumulated preferably in the outer part. This confirmed reports of Ferraz and Zöttl (1979), Koeppe (1981), Kloke (1983), Raisch (1983) and Zöttl (1985). Pb levels in the \_outer bark of the trees were similar at both sites. On the other hand, Trüby and Zöttl (1988) reported an accumulation of Pb at the trunk base of the tree from the mining spoil. Cadmium, as well as Zn, showed a completely different picture. The contents of both metals in bark of trees from the unpolluted brown earth. The results suggest a transport of these metals into bark, even though the extent might not be high under less polluted conditions.

Trüby and Zöttl (1989) described, that under moderate supply most of the Zn, which is transported into the bark is stored in living cells of the inner bark. Under conditions of very high supply, however, there is no significant accumulation of Zn in bark. For Cd they reported a possible washing off by rain from the bark, influencing metal levels in this tissue.

Airborne substances, like dust particles, can accumulate on bark surface in amounts depending on the time of exposure. Heichel and Hankin (1972) reported considerably higher levels of Pb in bark of older branches of white pine *(Pinus strobus)* than in bark of younger twigs from the same tree.

For the eastern part of Germany Gustke (1991) reported the results of a large-scale study of the distribution of several elements in bark of *Picea abies* and *Pinus vylvestris*.

Samples were collected from a screen net  $(10 \times 10 \text{ km})$  all over the territory, and were analyzed for a variety of elements, including Fe, Mg, Mn, Al and Zn. Regional distributions of the metals in bark of trees showed a close relation to polluted areas.

In Austria bark samples of *Picea abies* have been collected from about 250 trees in northern and eastern Tirol, beginning in 1982 (Herman 1991). Correlations were found between the traffic density on roads and levels of Pb and Cd in bark of trees.

Concentrations of Pb in bark and wood of Aleppo pine (*Pinus halepensis*) in the region of Athens, Greece, were determined by Karandinos et al. (1985). They found considerably higher levels in bark of trees growing in the city or in industrial areas than in those of parks or suburban areas. Concentrations were also higher in samples of trees near roads, than in those of greater distance from the roadside. Moreover, different concentration levels were observed depending on traffic density as well as on the presence of filtering vegetation. In addition, they divided bark samples in different layers, with a thickness of about 3 mm each. The concentration of the outermost bark was more than 20 times higher than that of inner layers (Fig. 3).

Such results underline the importance of standardization of sample thickness, as explained in Section 26.3.3.



**Fig. 3.** Lead concentrations at various depths in bark of *Pinus halepensis* from different sites in the greater Athens region. All sites (1-8) were known as polluted. Consecutive layers of bark (A-G) were each about 3 mm thick, layer A being the outermost bark surface. Sites of the trees: (1, 2) Egaleo-Iera Odos, (3-5) Dafni, (6) Mesogion street, (7) Tatoi, and (8) Dafni Alsos (adapted from Karandinos et al. 1985).

# **26.3** Advantages and Limitations of Biomonitoring with Tree Bark

With other methods of bioindication, several benefits and drawbacks should betaken into account, such as advantages and problems connected with the practical application of the technique, biotic and abiotic influences on the results and possible damages caused by the sampling method.

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#### 26.3.1 Advantages

The analysis of tree bark can provide information about the kind and degree of pollution, emission sources, and the average pollutant input over a long period of time for various elements. Particular advantages of the method are:

- Long term monitoring is possible, since the outermost parts of the tree bark are exposed to the atmosphere for a long time.
- The pollution of large areas can be investigated by collecting bark samples on a screen net basis (compare Gustke 1991).
- There is no limitation of monitoring by the season, as bark is available during the whole year.

- The determination of tree species is normally no problem (except in ecosystems like tropical rain forests). In other plant groups, like mosses or lichens, specialists of taxonomy have to be consulted.
- Collection of bark is definitely easy, especially when the sample is taken at breast height (Karandinos et al. 1985).
- The sampling technique should not affect the vitality of the tree, since only dead material is removed.
- Repeated sampling at the same tree is possible.
- The exposed bark as a means of biomonitoring is not endangered by wanton destruction, as may be the case with other materials, like standardized grass culture.
- Expenditure of time, personnel and material for collecting bark samples is comparatively low.

#### 26.3.2 Problems

#### 26.3.2.1 Biotic Influences (External and Internal)

Important influences of the biotic environment appear in the form of damage by animals, mostly insects (Stäxang 1969), for example, bark beetles, or bite of roes.

Covers of epiphytic organisms, like lichens, mosses and algae can influence the levels of trace metals in the outer part of the trunk. These plants are a sink for

"ace elements themselves (compare chapters of biomonitoring with those materials "In this volume).

An internal biotic factor, which may influence element levels in bark are species specific characteristics of bark types. The surface structure certainly affects uptake and movement of trace elements (compare Section 26.2.3). The extent by which an element is transported from the bark towards the inner portion of the stem is only little known. Such translocation processes probably depend very much on the physico-chemical properties of the elements and the anatomical structure of the bark. Several authors reported contradictory results. Koeppe (1981) assumed, that airborne Pb, deposited on the bark surface, is not, or only in very small amounts transported to the inner parts of the plant.

In contrast, Lepp and Dollard (1974a) proved this way of transport in a laboratory experiment. They used mature dormant branches of alder (*Alnus glutinosa*), beech (*Fagus sylvatica*), birch (*Betula pubescens*), elm (*Ulmus glabra*), horse chestnut (*Aesculus hippocastanum*), and lime (*Tilia europaea*), and applied <sup>210</sup>Pb on bark surfaces. In all species lateral translocation of Pb occurred. This transport was slow and, thus, probably non-metabolic (compare also Lepp and Dollard 1974b, Lepp 1975, Dollard and Lepp 1977).

Another internal factor, possibly influencing metal accumulation is the natural level of bark pH, which apparently depends on the species and the age of the tree (Stäxang 1969).

#### 26.3.2.2 Abiotic Problems

Stemflow, the run-off of rainwater from the crown down the bark to the ground, seems to be the most important source of error (Zöttl 1985a). Amount and composition of the downward running water depend on the crown architecture, i.e., the branching system, of the tree species as well as on the bark surface structure In beech (*Fagus sylvatica*) with a funnel shaped crown and a smooth bark, the extent of stemflow is stronger than in coniferous tree species, having more horizontal branches and a rather rough bark.

The effects of stemflow on trace element levels in tree bark are not yet clear, as pointed out, e.g., by Lepp (1975). Deposited elements can be washed off, resulting in a decrease of the mineral content. On the other hand, stemflow may transport large amounts of elements, deposited on the extensive surface of leaves and branches down to lower parts of the trunk. Thus, element levels may increase in bark of these regions.

Another possible effect might be a build-up of gradients of element concentrations on the trunk, with higher concentrations in lower regions (see Fig. 1).

Zöttl (1985) reported, that Cd concentrations in *Picea abies* bark from the Bärhalde, southern Germany, increased with declining stem height. Such data suggest a transport of Cd with stemflow. Differences in microclimate conditions of the trees' locations (i.e., for example different prevailing wind direction caused by nearby buildings or rocks), as well as the position of the sampled specimen in relation to other trees or the surrounding vegetation may cause serious problems, particularly if the number of collected samples is small.

In some investigations individual trees were found, that did not follow the general trend of monitored pollution, as was pointed out by Herman (1991). In this respect it may be advantageous, to collect a statistically significant number of bark samples from a group of trees at each particular site.

#### 26.3.2.3 Importance of Standardization

Standardization of sample thickness, orientation in relation to the prevailing wind direction, and height above ground are important requirements for future studies in biomonitoring with tree bark. This is necessary, to obtain comparable samples from trees of different sites.

The contents of Pb and Cd in the bark of trees depend on the height above ground (Szopa et al. 1973; Barnes et al. 1976; Zöttl 1985).

Reasons may be:

- Stemflow (see Section 26.3.2.2).
- Height and distance of pollution sources may affect the distribution of elements in bark (Hampp and Höll 1974; Lötschert and Köhm 1978).
- The lower the distance to the ground, the more important might be the influence of splashing water, especially in urban areas.

 Position of the tree, from which the samples are collected in relation to surrounding vegetation (closed canopy or solitary stand).

The height at which bark samples were collected varied in several investigations. Heichel and Hankin (1972) took bark samples from 75 cm above ground, Stäxang (1969) between 1.0 to 1.5 m, Hampp and Höll (1974) in 1.5 m, Grodzinska (1979) between 1.0 to 2.0 m. Lötschert and Köhm (1973a) as well as Kosmus and Grill (1986) collected bark between 1.2 to 1.6 m, Lötschert and Köhm (1978) at about 1.2 m above ground.

Not all species of trees are equally suitable for biomonitoring, as for example investigations by Okada et al. (1987) showed. They used bark of *Cryptomeria japonica* from differently polluted sites in Japan, which did not proof sensitive to changes in pollution.

Researchers should consider to use a defined tree species in studies of biomonitoring, to rule out influences of different kinds of bark. This would facilitate a comparison of results of different investigations.

However, several working groups in this field reported controversial results. Barnes et al. (1976) did not find considerable influences of different tree species on levels of Pb as well as of Cu and Zn in polluted areas, with the restriction of trees with very smooth bark, like white beam *(Sorbus aria)*.

On the other hand, investigations by Ward et al. (1974) showed different distributions of Pb in several tree species in New Zealand.

#### 26.4 Conclusions

Tree bark as a means of bioindication can be used for monitoring atmospheric pollution. Depending on the investigators' aims, the method was adapted to various problems:

(1) Determination of spatial distribution of trace elements in the environment on a local or regional scale. The most sensitive way should be by collecting samples on a screen net basis.

(2) Historical monitoring of temporal changes in the trace element pollution of a certain area. This can be achieved in different ways:

(a) Bark samples can be devided into small subsamples in radial direction. The age of the material decreases with its depth. An analysis of such samples may reveal a radial distribution pattern like those ones observed in annual rings in wood (compare Chapter 27, this volume). Some investigators tried to correlate such patterns with the history of trace element pollution over several decades.

(b) Another way of historical monitoring could be the comparison of analytical data of older investigations with more recent ones. In case, that data of older studies are not available, one may try to analyze bark material of trees that have been cut down in the past. If the outer bark was preserved and stored under dry conditions, a chemical analysis may still yield useful results.

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Bark analysis can, thus, give an indication of the degree of trace element pollution in various environments.

In urban areas monitoring of the extent of metallic air pollution levels with an assessment of danger for human health as done by Karandinos et al. (1975) could be useful.

In suburban ecosystems identification of local emitters and accumulations of trace metals in the environment for assessing possible future dangers of increasing concentrations for living organisms may be an important task.

Particular advantages of the method are its accuracy, the comparatively simple techniques and the low expenses required.

Problems and restrictions of the method arise mainly from a lack of standardization of techniques, insufficient knowledge of tree physiology as well as from some external biotical and abiotical factors, being beyond the control of the investigator.

Many of such problems may be avoided by standardization of the technique and a careful selection of the sample material (see Tab. 2).

Influence	Countermeasure	
radial gradients of element-concentration in bark	standardization of sample thickness	
possible radial transport of elements	element-specific studies required*	
characteristics of different tree species/ bark types	standardization of tree species and range of age of tree	
influence of stemflow	avoiding the affected areas of bark	
uneven (patchy) distribution of elements on bark surface	sampling of different parts of the stem to get an average value	
covering by lichens, algae mosses	careful selection of various parts of bark for sampling, to get an average value	
damage by animals	careful selection of individuals	
element-specific correlations between air pollution and bark levels	testing the suitability of the appropriate element, respectively exclusion if not suitable	
climate conditions	standardization of thickness, orientation with respect to the prevailing wind direction	
variation in data of different trees from same site	analysis of large number of individuals for cal- culation of average values	
data show no correlation with emissions	inspection of region between emission source and tree for filtering vegetation, air currents, etc.	

Tab. 2. Practical Suggestions and Measures against some Causes of Error in the Results of Biomonitoring with Tree Bark

\* compare Section 26.5

An inevitable restriction is the fact, that several elements may not be suitable in this respect. Particularly some of the more mobile ones have to be a excluded (compare Section 26.2.2).

Although several problems remain to be solved, the method of bark analysis for biomonitoring trace element pollution appears to be useful tool in the assessment of environmental hazards caused by potentially toxic elements.

#### **26.5** Recommendations for Future Research

Even though the method of biomonitoring with tree bark itself seems well developed and was often used with good success, a number of open questions remain to be resolved.

A major problem seems to be the obvious lack of quantitative information about radial movements of elements in tree bark. It is not clear, to what extent superficially deposited elements may penetrate the outer layers of bark. This certainly depends on the bark type and tree species as well as on chemical properties of the deposited compounds. An interesting and promising approach seems to be the work of Lepp and Dollard (1974a, b), who applied labelled Pb on surfaces of young branches and followed its movement in radial direction. Such investigations should be extended to other elements and older trees, to enable a direct comparison with analytical data of biomonitoring studies.

Besides an inward transport of superficially accumulated minerals, also element movements in an outward direction are conceivable. Minerals taken up by the roots or absorbed through leaf surfaces are distributed via xylem and phloem within the tree. Such elements can also reach the inner parts of the bark. Toxic minerals (e.g. Cd or Pb) or elements of ample supply (e.g. Ca or Mn) may be incorporated in the dead tissue of the bark to be released to the environment, when the tissue is finally shed. Thus, the contents of certain elements in bark may partly be due to root uptake, which will confuse an interpretation of analytical data of bark in terms of airborne deposition. Such conditions call for an investigation with labelled elements or microanalytical techniques (PIXE, etc.) in order to clarify the exact

locations as well as the mobility of elements in bark. Attention should also focus on effects of stemflow on element concentrations in bark, demonstrated by, e.g., Zöttl (1985a). Regions of the stem affected by stemflow must be recognized and avoided during the sampling process.

In many reports published so far, no distinction was made between nutrient elements, required for physiological processes, and toxic elements without any known function in the organism (compare Tab. 1). A clear separation seems essential, since the tree as a living organism may treat such elements in different ways. This will, in turn, influence the incorporation of minerals in bark.

Apparently, physiological studies are required to clarify the mobility of elements within the bark as well as to quantify exchange processes between bark and wood or the outer environment, respectively. Such information will faciliate future research in the field of biomonitoring with bark.

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