

Heavy metal concentrations in oak wood growth rings from the Taunus (Federal Republic of Germany) and the Valdivia (Chile) regions*

F. Queirolo^{1,*}, P. Valenta¹, S. Stegen¹, and S.-W. Breckle²

¹ Institute of Applied Physical Chemistry, Research Centre (KFA) Jülich, P. O. Box 1913, D-5170 Jülich, Federal Republic of Germany

² University of Bielefeld, Faculty of Biology, Bielefeld, Federal Republic of Germany

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Summary. Using a voltammetric procedure described previously, the radial distribution of Cd, Cu, Pb and Zn in annual growth rings of oak from two regions has been investigated: an unpolluted region in Valdivia (Chile) and a polluted region in Königstein (Taunus, FRG). The very low metal levels found in oak wood from the Valdivia region have necessitated that the method be improved and its accuracy tested with standard reference materials and by comparison with electrothermal atomic absorption spectrometry as an independent method. The radial distribution of the four metals investigated is similar in oaks from both regions. No significant differences have been observed in the average concentrations of the essential metals Zn and Cu in the oak tree rings from the two investigated regions. For the toxic metals Cd and Pb, however, a significant increase by a factor of 2 for Cd and by a factor of 12 for Pb has been found when comparing the Königstein and the Valdivia regions. This is evidence of expected pollution of the Königstein region by Pb and, to a lesser extent, by Cd since 1940 or earlier. The trees in both regions can be classified as sound (damage degree 0–1 in Königstein).

Key words: Cadmium – Growth ring – Heavy metals – Lead – Voltammetry

Introduction

Heavy metals originating from different natural and anthropogenic sources have contributed greatly to environmental pollution over the past few decades. A substantial portion of the total amount of some toxic heavy metals released from anthropogenic sources into the en-

vironment is emitted into the atmosphere. Therefore, a significant pathway for heavy metal pollution of terrestrial and aquatic ecosystems goes through the atmosphere, whence after transport both wet and dry deposition occurs (Georgii et al. 1986). It has been shown that up to 90% of toxic trace metals can be directly dissolved in rain water and are therefore deposited in a form very suitable for subsequent uptake by vegetation (Nürnberg et al. 1982).

According to information provided by the government of the Federal Republic of Germany on forest damage in 1984, approximately 3.7 million ha, or about 50% of the total forest area in Germany, has been visibly damaged. Oak trees were showing rapidly increasing damage (15% in 1983, 43% in 1984). It should be noted that oak, pine and beech are considered important trees because they control the stability of relevant forest ecosystems. These trees cannot be replaced by other tree species (BMELF 1984) without affecting this stability. Additionally, the usefulness of oak for the study of chronology of heavy metal pollution in forest areas has been demonstrated (Breckle and Wickern 1983).

Toxic substances deposited in the forests as wet deposition, dry deposition and interception by the tree canopy eventually accumulate in the soil. Thus, contamination by toxic substances can influence the growth and the quality of the tree either directly via uptake by leaves, trunk and buds, or indirectly via accumulation in the soil and the subsequent uptake via the roots. In the case of heavy metals, the latter pathway is the most important one (Jastrow et al. 1980; Lamoreaux and Chaney 1978).

The mechanism and extent of binding of heavy metals in the soil depends on soil composition because dissolved metals can exist as different species (Brümmer 1986). From the ecological point of view, the heavy metal content in the solution phase plays the most important role as the plant readily takes up metals in their dissolved form. Unfortunately, the processes that control the distribution of the various forms of metals in the soil, such as their speciation, have not yet been clarified. Important reactions of heavy metals, such as precipitation/dissolution, adsorption/desorption, formation of complexes and ion pairs, de-

* Attached to the Institute of Chemistry, Universidad del Norte, Antofagasta, Chile; material taken in part from Ph. D. Thesis, University of Bonn

pend on the pH value and are controlled by respective changes in the soil, e.g. in water content, in micro-organism activity and in the composition of the soil environment. All these processes influence the distribution of metal into various species, in both the solid and in the liquid phases of the soil.

It has been reported that, in 1987, 2–5 kmol of acid equivalents (H_3O^+) per ha were deposited in the pine forests of the state of Hessen (HFV 1988). These quantities of acid are much larger than the respective buffer capacity of the soil in this region. Thus, it can be expected that various physical, chemical and biological changes in the soil will result. Even a soil pH of 4.2 can substantially enhance the toxicity of heavy metals contained in the soil. The extent of forest damage in the state of Hessen in 1987 was the same as in 1986, and amounted to 48% of the total tree population. However, damage to oaks older than 60 years and to beeches has substantially increased, whereas damage caused by yellowing, mould and insects was only observed to a limited extent.

Taking into consideration the problems mentioned above, we have undertaken a detailed comparative study of the heavy metal concentrations in annual growth rings originating from two regions. The region of Königstein in the Taunus (FRG) is known to have been exposed for many years to contamination by heavy metals and, simultaneously, to acid rain. On the other hand, the trees originating from the region of Valdivia (Chile) have grown under natural conditions without any contamination by heavy metals from anthropogenic sources and a very low geographic background. There is no large industrial activity in this region. Moreover, the prevailing wind direction is from north and west so that fresh humid air is brought from the Pacific ocean (Huber 1980). Until now no investigations about the heavy metal content in the rain have been carried out. The acidity of the rain water – determined in an open rain water sampler on a weekly basis – is approximately pH 6.2–7.0 (Schlatter et al. 1987).

Materials and methods

Equipment

Tree ring samples were taken with a stainless steel incremental borer coated with Teflon to prevent heavy metal contamination. Tree cores were divided into 1-year increments using precision knives and stainless steel blades with the aid of a measuring microscope. Voltammetric measurements were performed in a semi-automated manner with a polarographic Analyzer PAR Mod. 264 A connected to a Static Mercury Drop electrode PAR Mod. 303 A (drop size large) as the working electrode and a Stirrer PAR Mod. 305. A saturated Ag/AgCl electrode was used as the reference electrode and a Pt wire as the auxiliary electrode. Voltammograms were recorded with a Hewlett-Packard Recorder Mod. 7045 A.

Chemicals

All the chemicals used to prepare standard solutions of the acid mixture for wet digestion and for the acidification of the solution in a voltammetric cell were Merck, Suprapur. Pure water was obtained by passing deionized water through a "Milli-Q-Water purification System" from

Millipore (Bedford, Mass., USA). The purity of water was checked daily before starting voltammetric determinations. Further details regarding the equipment, chemicals and purification procedures used are given elsewhere (Queirolo and Valenta 1987).

Wet digestion

Approximately 10–150 mg of wood (dry weight) corresponding to an individual oak ring were weighed and put into a conical quartz 5-ml cup. According to the quantity of wood, 0.3–0.8 ml of 65% HNO_3 and 0.1–0.2 ml of 70% HClO_4 were added. This mixture was covered with a quartz watch glass and heated gently at 100°C for 60–180 min depending on the quantity of wood. During this first digestion stage, the sample foams while rapidly dissolving, and care must be taken so that losses are avoided. After foaming has ceased, the temperature is elevated to 200°C and the mixture is heated until the evolution of nitrogen oxides is finished and a colourless or light yellow residue solution results. If the residue remains black or dark brown, more HNO_3 has to be added and the procedure repeated. When the HNO_3 has evaporated the temperature is raised to 250°C – without removing the quartz cover – and finally to 300°C, until the mixture completely evaporates. Ostapczuk et al. (1987) reported that complete evaporation must only be performed when the trace metal level is extremely low ($<10 \mu\text{g kg}^{-1}$). In our case, concentrations of Cd and Pb sometimes reached this low level.

There is no risk of explosion with the wet digestion described, as only minute quantities of HClO_4 are used. The residue in the quartz cup is cooled to 50°C and is dissolved in 1 ml pure water and 10 μl HClO_4 ; the elevated temperature is maintained for 15–20 min. Then the liquid is sucked out of the cup, transferred to a 5-ml polyethylene flask, weighed and 5 ml pure water is added. The final solution should have a pH of 1.2–1.5 and is ready for voltammetric determination.

Voltammetric determination

Two millilitres of the analyte resulting from wet digestion is added to a voltammetric cell and filled with pure water to a volume of 5 ml to obtain pH 1.8–2.0. The solution is deaerated with pure nitrogen (99.999%) for 4 min and the heavy metals Cd, Pb, Cu and Zn are determined simultaneously using differential pulse anodic stripping voltammetry. During the deposition stage, a potential of –1.2 V is adjusted and the solution is stirred with a magnetic stirrer for 15–180 s depending on the Zn concentration in the analyte. For Cd and Pb determination, the optimal deposition time is 180–300 s. With an elevated Zn concentration, determination in two steps is recommended. At first Zn is determined in the potential range –1.2 to –0.8 V using a deposition potential of –1.2 V and then Cd, Pb and Cu are determined in the potential range of –0.8 V to +0.3 V using a deposition potential of –0.8 V. After a resting period of 30 s, the heavy metals are measured in a quiet solution in the differential pulse mode with the following parameters: pulse height 50 mV, pulse duration 56 ms, clock time 0.2 s and scan rate 10 mV s^{-1} . If the metal concentrations in the sample differ greatly, a change in the current range after the Zn peak and/or the Pb peak is necessary to obtain sufficiently large signals. The unknown metal concentration in the sample is determined using the standard addition method. In this manner, small differences in the composition of the analyte solution which might influence the peak height are eliminated. The voltammogram of the sample solution is registered twice and then voltammograms of the first, and eventually, also the second standard addition follow. An example of the voltammetric determination of heavy metals in the analyte of a wood sample is given in Figs. 1 and 2.

Precision and accuracy of the method

The precision and accuracy of our method has been tested via comparison with the electrothermal atomic absorption spectrometry (ETAAS) and standard reference materials. In Table 1, the trace metal determina-

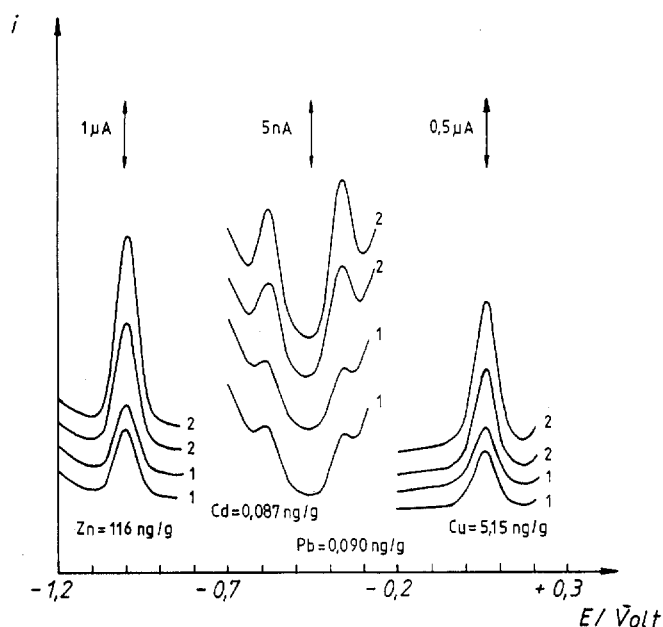


Fig. 1. Voltammetric determination of the heavy metals Zn, Cd, Pb and Cu in an analyte resulting from the wet digestion of an individual growth ring of oak (*Quercus robur*). Oak no. 3, year 1976. Sample weight 0.06689 g; differential pulse anodic stripping voltammetry, pulse height 50 mV, scan rate 10 mV s⁻¹, clock time 0.2 s, deposition time: for Zn 30 s at E_d -1.2 V, for Cd, Pb and Cu 300 s at E_d -0.8 V. Curves 1 (sample), curves 2 (first standard addition). Total time of the simultaneous determination 50 min

tion in the NBS material 1571 "Orchard leaves" has been shown for six independent determinations. The concentrations of all four investigated metals lie well within the certified values. The precision of voltammetric determination indicated as relative SD lies below 10% and is, in general, better than that of the ETAAS.

Sampling regions

In order to estimate typical concentrations of the heavy metals Cd, Pb, Cu and Zn in wood, samples from seven oaks in the Valdivia region and five oaks in the Königstein region were taken and heavy metal concentrations determined in individual growth rings. Samples were taken from sound living oak trees. In Valdivia the species *Q. robur* was used, in Königstein, the species *Q. petraea*. These oak trees exhibit ring-porous wood and other advantageous properties for this type of research (Breckle and Wickern 1983; Bosshard 1984; Baes 1985; Hagemeyer 1985). Moreover, the annual growth rings can be well separated and differentiated. Sam-

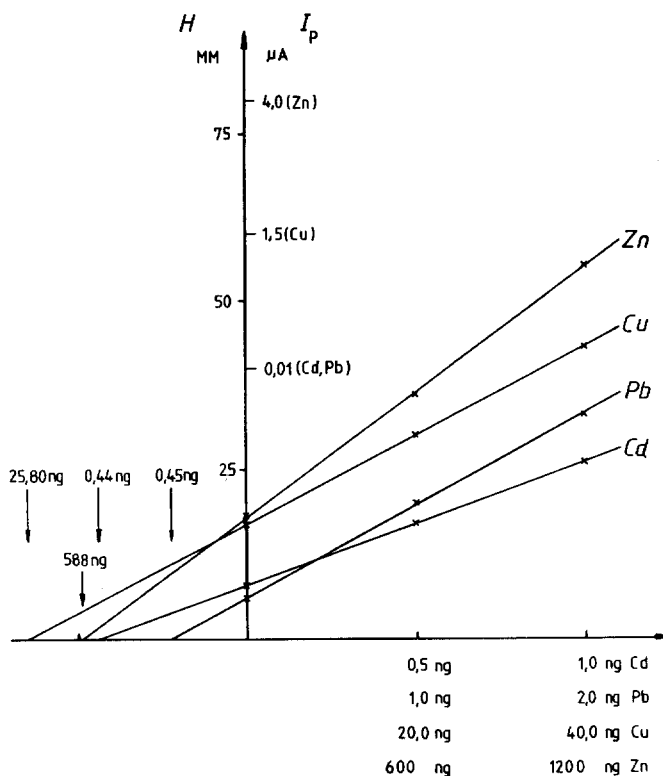


Fig. 2. Evaluation by the standard addition method

pling was performed at the end of May 1985 in the Königstein region and in January 1987 in the Valdivia region. The cores obtained in the Königstein region enabled heavy metal concentrations to be determined back to 1940. In the Valdivia region, however, the tree rings are much thicker. Thus the bore cores of the corresponding length comprised fewer tree rings and heavy metal determinations were only possible back to 1962.

Valdivia region. The city of Valdivia is situated in the South of the Republic of Chile at an altitude of 9 m above sea level. Owing to its relative proximity to the sea and to a large hydrogeographic basin formed by the Valdivia and Cruces rivers, it possesses a climate characteristic of oceanic regions. Annual precipitation is 2500 mm. The pH range of rain water sampled over a 1-week period with an open sampler was 6.2–7.0 (Schlatter et al. 1987). The average temperature is 12°C, with an annual oscillation of 9.2°C (Montaldo 1983). The annual relative humidity averages approximately 77% (April to August 80%–90% and December to February 60%–70%). The growing season lasts – taking into account days with temperatures above 10°C – from September to May

Table 1. Determination of Zn, Cd, Pb and Cu in biological reference materials by two independent methods, differential pulse anodic stripping voltammetry (DPASV) and graphite furnace atomic absorption spectrometry (GFAAS)

Sample	Element	Values found (μg/g)				Certified values (μg/g)
		DPASV	RSD (%)	GFAAS	RSD (%)	
Orchard leaves	Zn	25 ± 2	(8)	22 ± 3	(19)	25 ± 3
NBS 1571	Cd	0.11 ± 0.01	(9)	0.13 ± 0.01	(8)	0.11 ± 0.01
n = 6	Pb	41 ± 2	(5)	40 ± 3	(8)	45 ± 3
	Cu	12 ± 1	(8)	10 ± 1	(10)	12 ± 1

n = Number of independent determinations; RSD = Relative standard deviation

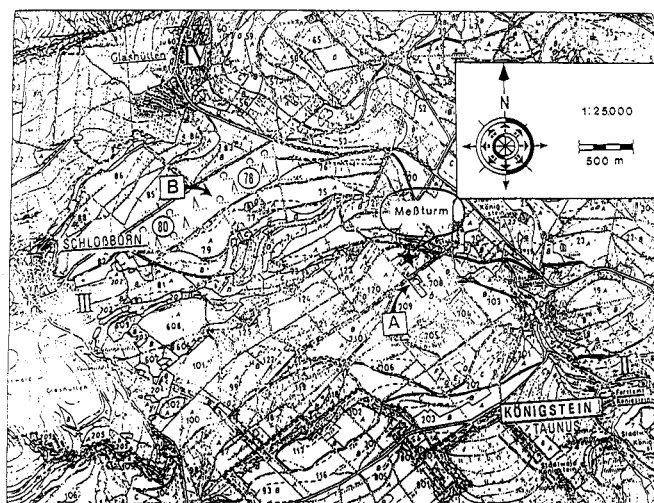
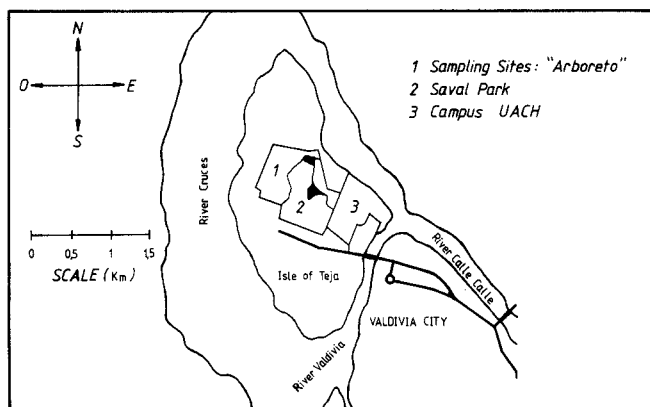


Fig. 3. Location of sampling sites of trees and soil: **a** Arboreto region, Republic of Chile (R. Grez, personal communication, 1987); **b** Königstein A region

(259 days). The place from which the tree and soil samples were taken corresponds to the region named "Arboreto" and belongs to the Universidad Austral de Chile (Fig. 3). It should be noted that the soil where trees are growing was not fertilized. The soil found at the sampling site and on its slope is of recent volcanic origin (quaternary), with the fourth degree of intermixing with soils derived from metamorphic rocks (in minor or feeble proportion; R. Grez, personal communications, 1987). This soil is very porous, has good internal drainage and a fine medium texture. Depending on the depth, the soil varies from silt to clay at the surface and sand to silt with clay at approximately 70 cm depth.

Königstein region. A detailed study of the wet deposition of heavy metals with atmospheric precipitates was launched in 1980 to elucidate heavy metal atmospheric pollution trends in the Federal Republic of Germany (Nürnberg et al. 1984). An automatic rain water sampler in the Königstein region was added to the already existing network of approximately 20 in 1981. Elevated levels of heavy metals in rain water have been found in this region since sampling was begun, as well as elevated acid levels in rain water [a mean monthly precipitation of 3.1 mg of H_2O , + per $m^2/month$ (Kraemer et al. 1985)]. Therefore, this region was chosen as a typical forst region polluted by heavy metals. The state of Hessen is mountainous and therefore experiences rapid changes of weather. The sampling site has the following properties (HAFFA 1985): (1) growing zone: mixed oak forest zone at a level of 500 m; (2) climatic humidity: feebly subatlantic with an average annual precipitation of 250–500 mm during the forst growing season (May–September) and a temperature of 11–17°C; (3) water supply: moderately fresh; (4) trophic type: mesotrophic; and (5) soil type: clayey schists with loessic to sandy loam.

Table 2. Acidity of the soil in Valdivia and Königstein regions, determined in a mixture soil/solution in the ratio of 1 : 2.5

Depth of the sampling site (cm)	pH (H_2O)		pH (1 M KCl)	
	Valdivia	Königstein	Valdivia	Königstein
0– 5	4.8	3.27	4.4	2.8
10– 15	5.1	3.4	4.5	3.0
35– 40	5.0	3.6	4.9	3.5
70– 75	5.0	3.3	4.8	3.0
100–105	5.0	a	4.8	a

^a Owing to the hardness of the soil it was not possible to take samples

Soil characterization

Soil sampling was performed at the same time as tree ring sampling. The soil samples are not representative of the whole "Arboreto" region. However, they can provide a good estimate of the character of the soil where the oaks grow. Soil samples were taken in an oak forest at a distance of about 2 m from the trunk. In every sampling site approximately 1 m^3 of soil was removed. In Königstein the sampling could only be performed down to a depth of 70 cm because of the hardness of the soil (50% rock). In order not to contaminate soil samples with heavy metals originating from the instruments used for sampling, the soil levels chosen were reached by removing soil horizontally and using plastic shovels to a depth of 5 cm. In this manner, rectangular soil samples were taken and then homogenized at the levels of 0–5 cm; 10–15 cm; 35–40 cm; 70–75 cm and 100–105 cm. This procedure was repeated for every pit. The homogenized soil sample was dried at 100°C, milled and then aliquoted for the respective determination. The acidity of the soil samples taken in both regions is summarized in Table 2 and the heavy metal concentrations in the soil are listed in Table 3.

Results and discussion

Typical metal concentrations in annual growth oak wood rings originating from the Valdivia region and the Königstein region are shown in Figs. 4 and 5.

In Fig. 4 (I–IV), the concentrations of Zn, Cu, Cd and Pb in individual growth rings of oak no. 3 from the Valdivia region are shown for 1962–1986. This sample was chosen as a typical specimen of oak and our results thus reflect general trends in metal concentrations in trees from this region. There was no noticeable difference between the concentrations found in heartwood and in sapwood, corresponding to maximum and minimum values, during the period under investigation. The most important concentration increase is generally found in the outer growth rings bordering the cortex, i.e. in the first to the fifth ring corresponding to the 5 most recent years. The other concentration maximum appears for the majority of the trees in the transition zone between the heartwood and the sapwood. However, the latter maximum is not as distinct as the former one – with exception of Cu. The maximum in the external growth rings has also been observed by other investigators, both for essential and toxic heavy metals (Clement and Janin 1976; Schroeder and Balassa 1963). Other authors (Ault et al. 1970; Rolfe 1974) have observed an increased content of Pb isotopes in the most recent areas

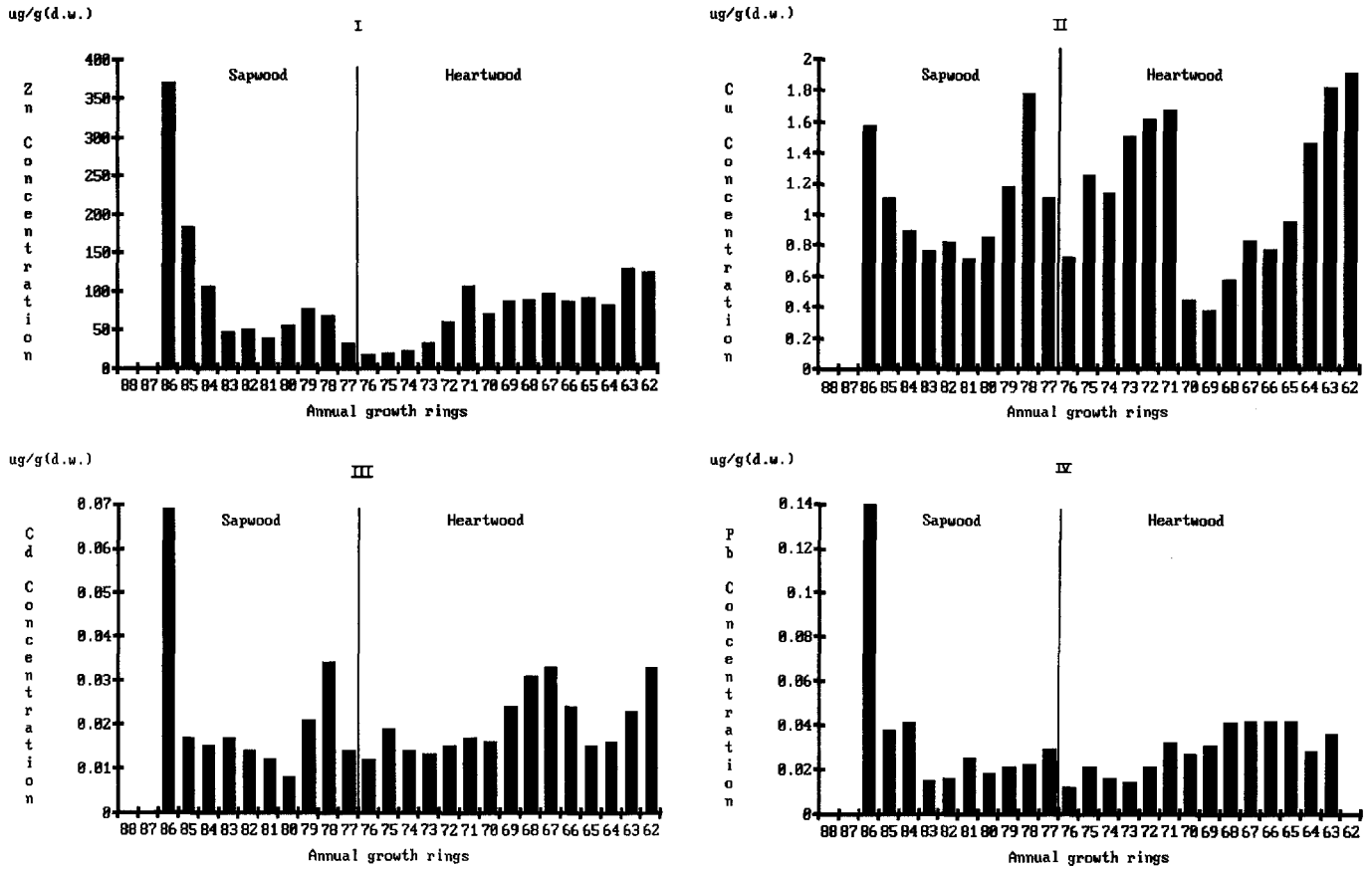


Fig. 4. Heavy metal concentrations in an oak tree depending on the radial distance, indicated as annual growth rings. *Q. robur*, no. 3 from the Valdivia region (Chile). Average standard deviations (SD) are indicated: I–Zn (SD 6%), II–Cu (SD 10%), III–Cd (SD 10%), IV–Pb (SD 11%)

of the trunk and have discussed the possible radial displacement of that metal. In other investigations, a possible exchange of Pb between the cortex and the most external growth rings has been proposed (Lepp and Dollard 1974). Also, a possible displacement of heavy metals between the adjacent growth rings has been discussed (Hagemeyer 1985).

It should be noted that the secondary phloem exhibits an influence on the most recent growth ring situated in its immediate neighbourhood. As can be seen from Fig. 4 (III–IV), the metal concentrations for the first annual growth ring rise steeply to high values. This may be caused by the fact that during the separation of annual growth rings a part of the secondary phloem was taken together with the adjacent ring so that the concentration determined corresponds to a mixture of both parts of the trunk. Alternatively, increased metal concentrations in the most recent growth rings may also be due to natural causes, as the principal transport of water and nutrients proceeds in the most external part of the trunk. Analogous investigations on pines have revealed an increased concentration of phosphate in the external growth rings. This can be explained by the role which the phosphate anion plays as an essential anion for the biological processes in plants. In fact, this anion has also been proposed as a marker for the assessment of biologically active parts of the tree (Maurer

et al. 1986). However, increased concentrations of chloride and sulphate were not found by these authors, and it was thus concluded that these anions are not essential for the plant. As can be seen in Fig. 4 (I–IV), increased metal concentrations in the external growth rings are exhibited for all the metals investigated, essential (Zn and Cu) as well as toxic (Cd and Pb).

The following conclusions may be drawn based on the comparison of the average values of metal concentrations in growth rings originating from six oaks from the Valdivia region and six oaks from the Königstein region, as shown in Fig. 5 a and b. For the essential metals Zn and Cu, no relevant differences in concentrations between the two regions are observed despite climatic differences between the two regions, genetic differences between the two oak species, and different levels of soil acidity. However, for the toxic elements Cd and Pb, significant differences in average concentrations (*C*-values) can be seen. The average Cd concentration is about twice as high in the Königstein region as in the Valdivia region (Fig. 5 b, III). The elevated values for both regions in the most recent tree rings (*A*-values) are probably caused by not fully complete separation of wood and phloem in the samples. The average value of Pb concentration in the Königstein region is approximately 12 times as large as the concentration in trees from the Valdivia region.

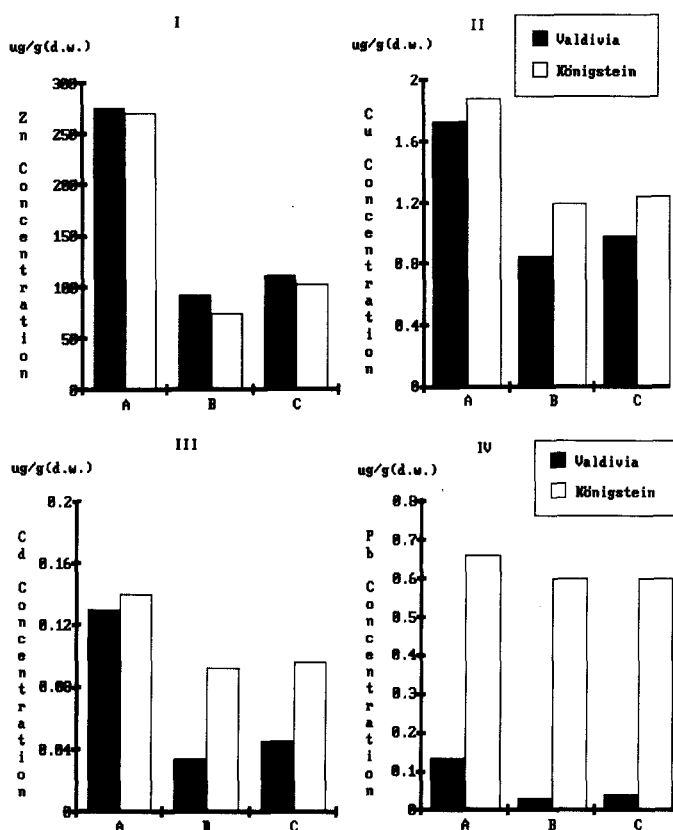


Fig. 5 a, b. Mean metal concentration in oak tree rings from the Valdivia region (6 trees) and from the Königstein region (6 trees). A, Mean concentration in the recent rings (last 5 years); B, mean concentration in the older rings (older than 5 years); C, overall mean concentration. a Zn (I) and Cu (II) concentrations; b Cd (III) and Pb (IV) concentrations

Taking into account that the investigated oak trees are living and sound (damage degree 0–1), the increased Pb and Cd concentrations clearly indicate that a noticeable pollution by the mentioned heavy metals has prevailed in the Königstein region during the period of observation, i. e. since 1940. These differences can be explained by higher Cd and Pb concentrations in the soil of Königstein, particularly in its superficial layer (see Table 3). In this humus layer heavy metals are bound rather strongly to humic and fulvic acids, i. e. to their carboxylic and phenolic functional groups. The Cd content of 0.4 ppm of Cd is taken as normal for a non-polluted region (Berrow et al. 1984). For Pb in soil the concentration range 2.5–85 ppm is taken as normal for unpolluted soils with an average value of 30 ppm in the humus layer. The soils with a Pb content above 100 ppm are without doubt contaminated with Pb (Davies 1986). Increasing soil acidification can lead to increasing mobilization of heavy metals (König et al. 1985). However, this effect is mainly noticeable for Cd. In a recent study of the mobilization of heavy metals in forest soils having a pH range of 2.9–3.7 only a marginal Pb output with seepage has been found for Pb (Schultz 1989). Thus, it can be concluded that the elevated concentrations of Cd and especially of Pb in the soil of Königstein, particularly in its superficial layer, result to a major extent from the deposition of heavy metals by atmospheric precipitates.

Table 3. Heavy metal concentration in the soil (in ppm dry weight) determined after the wet digestion in aqua regia (standard procedure)

Depth (cm)	Valdivia (Chile) ^a				Königstein (FRG) ^b			
	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu
0– 5	65		8	41	51		133	16
10– 15	62		8	48	36		50	8
35– 40	63	≤ 0.1	9	58	45	≤ 5	20	6
70– 75	58		10	59	28		20	8
100–105	57		10	60	–	–	–	–

^a Analysis was performed at Hessische Landwirtschaftliche Versuchsanstalt and at Landwirtschaftliches Untersuchungsamt Kassel-Harleshausen

^b Analysis was performed at the Central Laboratory for Chemical Analysis of the KFA Jülich

The differences in the concentrations of the essential metals Cu and Zn are, on the other hand, not significant and lie within a natural fluctuation. As natural (geographic) sources of Cd and Pb are normally extremely low in Germany, it may be concluded that this type of pollution comes from anthropogenic sources, e. g. gasoline for Pb. This observation agrees with the elevated values of Pb and Cd found in rain water in Germany. The concentration of Cd and Pb in fresh arctic snow (Mart 1983), as compared with the background concentration of those heavy metals in rain water in Germany observed since 1980 (Nürnberg et al. 1984; Valenta et al. 1986), is a factor of 1000 larger in Germany than that found in the unpolluted Arctic region and even more when fossil arctic ice is taken for comparison.

A noticeable increase in Cd and Pb concentrations in the most recent growth rings has been observed since about 1970 in the Königstein region. The same trend has been observed in other individual oak samples from this region. However, if the average of a number of oak species is taken, as a general conclusion it can be stated that throughout the entire observation period, from 1940 to 1986, Pb concentrations in Königstein remained more than an order of magnitude higher than those found in the unpolluted Valdivia region. It should be noticed in this context that the concentrations of heavy metals Cd and Pb in the oak trees of the Valdivia region lie in the order of magnitude of 0.05 µg/g (dry weight). These values are far lower than those indicated in the literature, and may be considered as base levels of those metals in an oak tree (*Q. petraea*).

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