



BIOMONITORING OF AIRBORNE INORGANIC AND ORGANIC POLLUTANTS BY MEANS OF PINE TREE BARKS.

I. TEMPORAL AND SPATIAL VARIATIONS

H. SCHULZ¹, P. POPP², G. HUHNS¹, H.-J. STÄRK², G. SCHÜRMAN¹

¹Department of Chemical Ecotoxicology

²Department of Analytical Chemistry

UFZ Centre for Environmental Research,
Leipzig, Germany

Abstract

Scots pine (*Pinus sylvestris* L.) bark samples were collected at two field sites (Neuglobsow, Rösa) and in different years between 1987 and 1996 in the east of Germany. The barks were analyzed with respect to the following inorganic and organic substances: Al, As, B, Ca, Cd, Ce, Cr, Cu, Fe, Hg, Mo, NH₄⁺, Ni, NO₃⁻, PO₄³⁻, Pb, Sr, SO₄²⁻, Ti, V, W, Zr, Zn, benzo(a)pyrene, fluoranthene, pyrene, α -hexachlorocyclohexane (α -HCH) and dichlorodiphenyltrichloroethane (DDT). In addition to bark samples from the site Rösa, 53 test sites were investigated in the Nature Park Dübener Heide. Here, the analysis of the barks aimed at discovering spatial patterns of the above-mentioned substances. Since 1991, most of the determined substances (e.g. sulfate, nitrate, calcium, lead, benzo(a)pyrene, α -HCH) show decreased concentration values in bark samples from both sites. Temporal variations reflect substantial infra-structural changes in eastern Germany, especially at Rösa and in the industrial region around the cities Leipzig, Halle, and Bitterfeld. Moreover, nitrate concentrations in barks are increasing since 1995. The trend can be explained with increased nitrogen emissions from motor traffic and livestock farms. Spatial patterns of sulphate and ammonia reflect inputs from power plants and agriculture in pine stands of the Nature Park Dübener Heide. The results show that barks of pine trees can be used as biomonitoring tools to indicate and characterize depositions of airborne organic and inorganic pollutants.

1. INTRODUCTION

Pine tree barks are excellent adsorbents of airborne pollutants, including anthropogenic heavy metals [1-2]. The bark surface is very porous, and the absence of metabolic processes makes it almost inert in the presence of inorganic and organic substances. Additionally, pine stands are widespread in Central, Northern and Eastern Europe. Therefore pine barks have proven useful as passive bioindicators for airborne pollutants [3-8].

Monitoring with pine barks supplies low-cost information on the composition and quantity of the deposition of pollutants. As shown recently, pine tree barks can also be used to quantify throughfall rates in pine stands [9]. While pine tree barks have often served as biomonitoring tool for airborne sulphate, calcium and heavy metals, there are only few studies with airborne organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and semivolatile organic compounds (SOCs). Moreover, there are only few field studies with pine barks on regional and supra-regional scales, which contrasts with the situation with mosses and lichens as bioindicators.

In the present study, pine barks are used to characterize temporal variations and spatial patterns of selected inorganic and organic substances, and the suitability of this biomonitoring tool is demonstrated by comparing contaminant loads in the bark of pine stands at two test sites with known low and high airborne pollution.

2. MATERIAL AND METHODS

2.1. Sampling and sites

Sampling was carried out in different years between October 1987 and October 1996. Bark samples were taken from 60 to 80 years old Scots pine trees (*Pinus sylvestris* L.) in the following areas: Neuglobsow near lake Stechlin about 70 km north of Berlin (Brandenburg, Germany), Rösa (Nature Park Dübener Heide) in the northeast of the industrial region Leipzig-Halle (Sachsen-Anhalt,

Germany), and in different background or reference areas of South Norway (National Park Jostalsbreen), Russia (Syktywkar) and Poland (Bialowieska). Additionally, the area of Nature Park Dübener Heide (Fig.1) was subdivided in a 2.5 x 2.5 km grid of 56 test sites to analyze spatial patterns of airborne pollutants. Using a hard steel knife, the external surface of barks was collected from the non-weather area at a height of 1.50-1.70 m above the ground. Samples from at least 25 pine stems from each test site were mixed, dried at 30°C, and milled in a contamination-free manner for further cleanup and analysis. For statistical calculations, each of the test areas was subdivided into five test sites. Each test site was represented by one mix sample of pine barks.

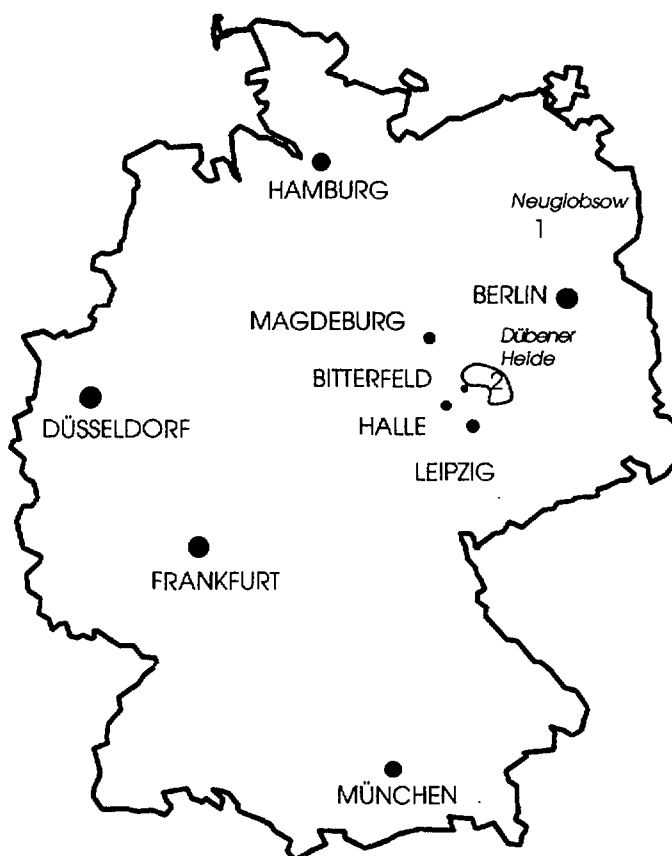


Fig.1 Map of Germany with location of test areas with sites for bark sampling in Scots pine stands. 1 - Neuglobsow (near lake Stechlin); 2 - Rösa (Dübener Heide).

2.2. Chemical Analyses

Anion concentrations (chloride, sulphate, nitrate, phosphate) were determined using an ion chromatograph (DX 500, Dionex). At ambient temperature, 0.5 g of bark samples were extracted with 25 mL deionized water for 45 min. A 50 mL sample was injected into the chromatographic system. The separation was performed on a IONPAC AS12A column (Dionex). The mobile phase consisted of 2.7 mM CO_3^{2-} /0.3 mM HCO_3^- solution. The flow rate was fixed at 1.5 mL/min. Ammonium concentration was measured using bark extracts (6.25 g bark/25 mL 1% K_2SO_4 w/w) with a gas-sensitive ammonia electrode (Type NH 500/2, WTW).

For the determination of heavy metals, 0.5 g of bark samples were digested with 5 mL concentrated nitric acid at 150°C and 1.2 MPa in a microwave digester (MDS 2000, CEM). Elemental contents in the digestion solution were analyzed using inductive coupled plasma atom emission spectrometry (JY24, Jobin Yvon) and inductive coupled plasma mass spectrometry (ELAN 5000, Perkin Elmer, Norwalk, CT, USA).

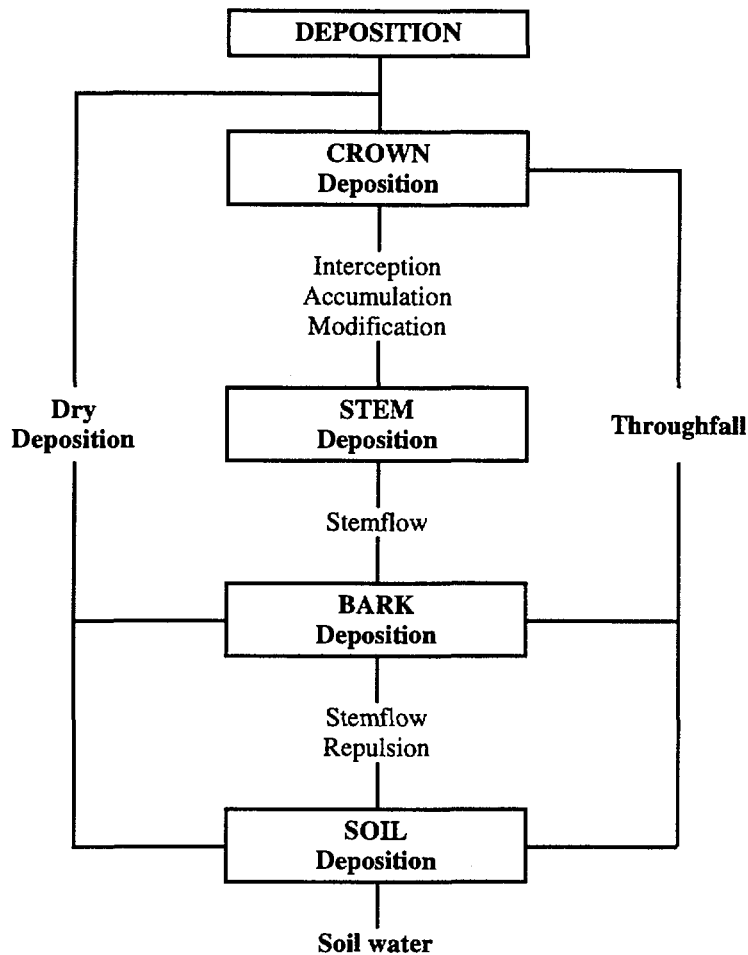


Fig.2 Survey of accumulation process in pine bark.

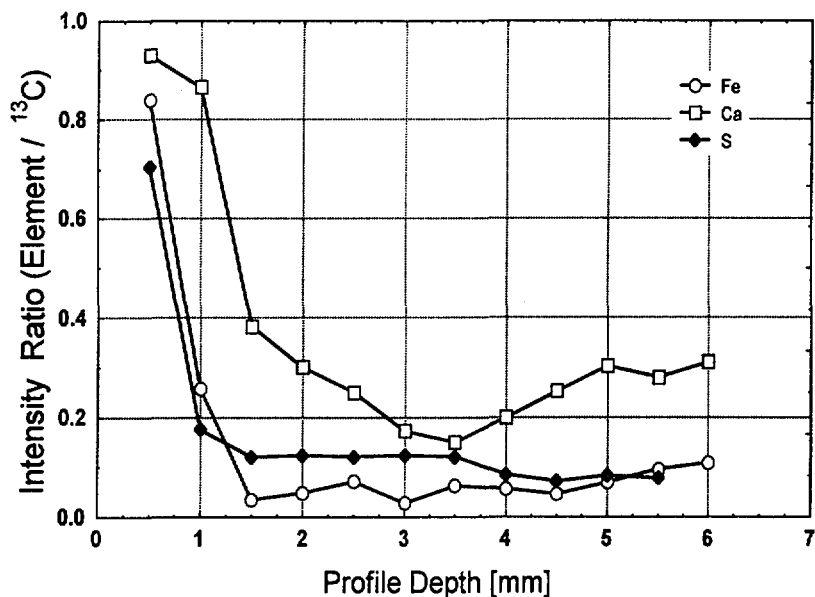


Fig.3 Result of a bark profile analysis that was performed with a Laser ICP-MS. The intensities of sulphur, iron and calcium were measured in 0.5 mm steps and were applied to ^{13}C as the inner standard. The 0.1 mm depth corresponds to the outer layer of tree (bark surface). The measure points represent mean values of three determinations.

TABLE I. CONCENTRATION OF INORGANIC AND ORGANIC SUBSTANCES IN BARK SAMPLES TAKEN IN THE EURO-PEAN COUNTRIES GERMANY, NORWAY, POLAND AND RUSSIA. THE CONTENTS ARE SHOWN AS MINIMA, MAXIMA AND BIOINDICATION INDEXES (MIN/MAX).

Element/ Compound	Minimum	Maximum	Bioindication Index
	($\mu\text{g g}^{-1}$ d.w.)		
Al	1	1500	1500
As	0.01	3.9	386
B	0.8	24	30
Ca	1800	27000	15
Cd	0.1	1.2	12
Ce	0.1	13.8	125
Cr	0.5	10.4	20
Cu	1	36	36
Fe	51	4794	94
Hg	0.001	1.180	1180
Mo	0.01	4.70	470
NH ₄ ⁺	20	3800	190
Ni	0.01	8.2	820
NO ₃ ⁻	1	800	800
Pb	1.7	61.2	36
PO ₄ ³⁻	25	150	6
Sr	4	92	23
SO ₄ ²⁻	30	57000	1900
Ti	3.2	372	118
V	0.04	13	325
W	0.01	1	100
Zn	4.50	189	42
Zr	0.03	6	200
Benzo(a)pyrene	0.0004	0.0210	50
Fluoranthene	0.0074	0.1332	18
Pyrene	0.005	0.083	17
α -HCH	0.008	0.120	15
DDT	0.019	0.304	16

The profile analyses were determined with a laser inductive coupled plasma mass spectrometer (LS 320-ELAN 5000, Perkin-Elmer). A nitrogen purged Laser-ICP-AES combination was used to measure the sulfur profile. A rubin laser (LMA 10, 1694 nm, Carl Zeiss Jena) for volatilization of the bark sample was coupled with a Spectroflame ICP-AES spectrometer (Spectro). The element distribution in the bark layers was measured in 0.5-mm steps starting from the surface. The amount of ¹³C was used as an inner standard for the different bark layers.

TABLE II. MEAN CONCENTRATIONS (\pm STANDARD ERROR) OF ELEMENTS AND COMPOUNDS IN BARK SAMPLES (N=5) FROM BACKGROUND AREAS (NATIONAL PARK JOSTE-DALSBREEN, NORWAY; SYKTYWKAR, RUSSIA), LOW POLLUTED AREAS (BIALOWIESKA, POLAND; NEUGLOBSOW, GERMANY) AND HIGH POLLUTED AREA (RÖSA, GERMANY). B(A)P - BENZO(A)PYRENE; α -HCH - α -HEXACHLOROCYCLOHEXANE.

Element/ Compound	Jostedalsbreen	Syktywkar	Bialowieska	Neuglobsow	Rösa
SO ₄ -S (mg g ⁻¹)	0.08 \pm 0.01	0.07 \pm 0.05	0.23 \pm 0.03	0.95 \pm 0.07	15.77 \pm 0.77
NH ₄ -N (mg g ⁻¹)	0.049 \pm 0.034	0.036 \pm 0.007	0.078 \pm 0.011	0.077 \pm 0.003	0.68 \pm 0.13
NO ₃ -N (mg g ⁻¹)	0.02 \pm 0.0001	0.001 \pm 0.0001	0.08 \pm 0.001	0.019 \pm 0.003	0.024 \pm 0.002
Ca (mg g ⁻¹)	3.49 \pm 0.34	2.98 \pm 0.17	6.11 \pm 0.36	3.01 \pm 0.31	21.03 \pm 0.86
Fe (mg g ⁻¹)	0.10 \pm 0.04	0.11 \pm 0.02	0.24 \pm 0.05	0.40 \pm 0.04	3.49 \pm 0.21
Al (μ g g ⁻¹)	0.39 \pm 0.06	0.31 \pm 0.03	0.48 \pm 0.02	0.28 \pm 0.02	1.09 \pm 0.05
Ti (μ g g ⁻¹)	6.3 \pm 2.2	7.2 \pm 0.4	16.1 \pm 1.4	9.1 \pm 1.1	241 \pm 14.9
Pb (μ g g ⁻¹)	1.9 \pm 0.1	2.2 \pm 0.1	4.5 \pm 0.3	15.2 \pm 1.7	20.9 \pm 1.3
Cd (μ g g ⁻¹)	0.2 \pm 0.001	0.2 \pm 0.001	0.4 \pm 0.001	0.2 \pm 0.001	0.3 \pm 0.001
Cr (μ g g ⁻¹)	1.1 \pm 0.4	0.8 \pm 0.1	3.1 \pm 0.2	1.4 \pm 0.2	7.1 \pm 0.4
V (μ g g ⁻¹)	0.3 \pm 0.1	0.8 \pm 0.1	1.5 \pm 0.2	2.4 \pm 0.2	10.7 \pm 0.6
B(a)p (ng g ⁻¹)	1.18 \pm 0.36	2.6 \pm 0.42	1.42 \pm 0.59	3.87 \pm 0.21	9.14 \pm 1.08
α -HCH (ng g ⁻¹)	-	-	-	27.0 \pm 3.2	100.3 \pm 9.8

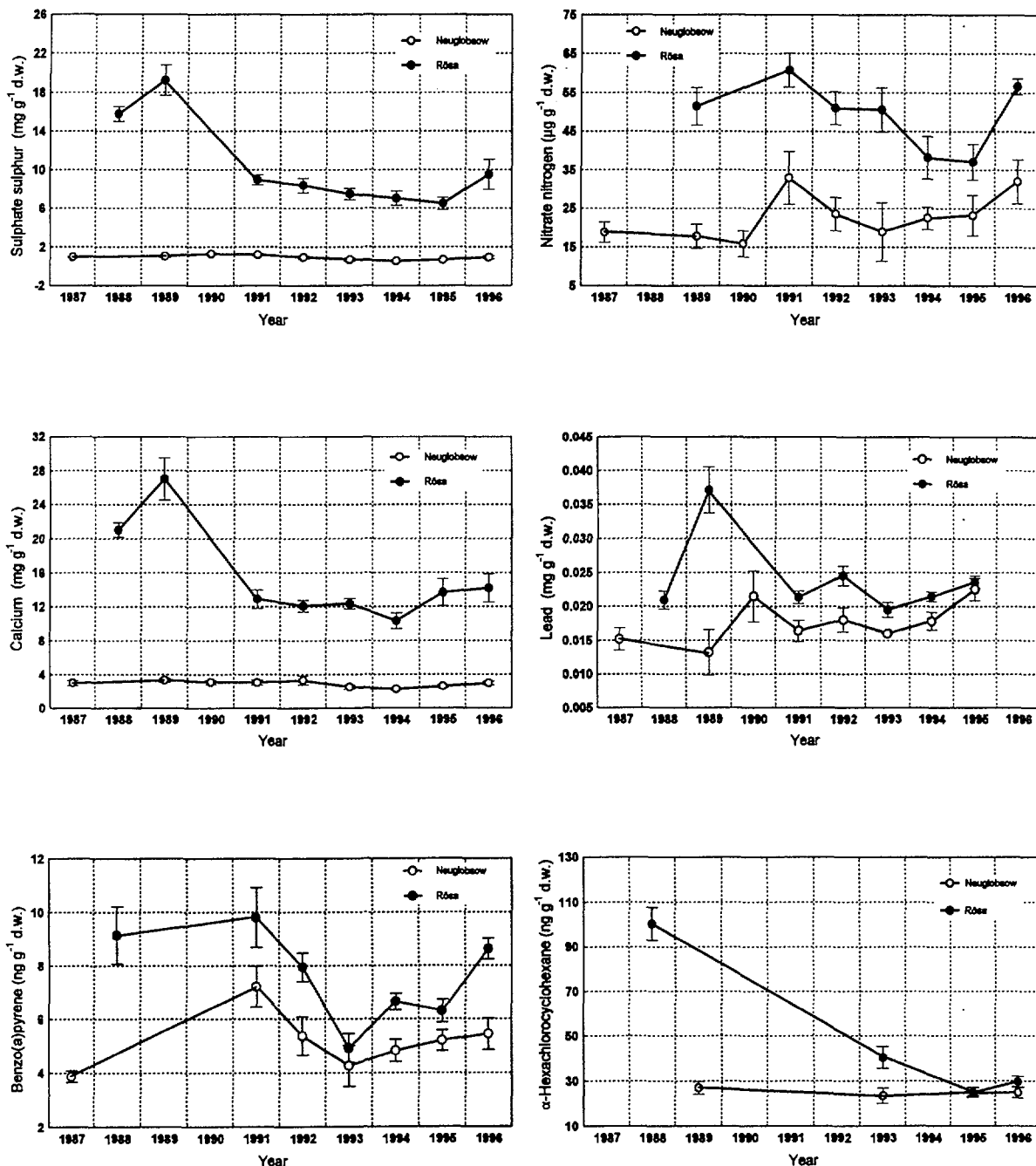


Fig.4 Seasonal variations of sulphate sulphur, nitrate nitrogen, calcium, lead, benzo(a)pyrene and α -hexachlorocyclohexane in pine barks from the sites Rösa and Neuglobsow between 1987 and 1996. The measure points represent mean values of 5 mix samples per test area with standard errors.

For the PAH analysis 5 g of bark samples were extracted with toluene and a solvent exchange to cyclohexane was carried out. After the samples were subjected to a silica gel clean-up and a final solvent exchange (acetonitrile). The determination was carried out with a HPLC system (System Gold, Beckmann) equipped with a programmable fluorescence detector (Shimadzu RF-551). The PAHs were separated on a Bakerbond PAH 16 Plus column (250x3 mm I.D.) with a pre-column at a temperature of 25°C. Eluent (A) was water, eluent (B) acetonitrile and the eluent programme started with 50% A and 50% B for 5 min, then the content of B was increased to 100% in 30 min with a linear gradient. This concentration was held constant for 10 min until the end of the analysis.

HCHs and DDX-compounds (SOCs) were determined with a HP 5890 II device (Hewlett Packard) with electron capture detection (ECD). The extraction of 3 g of bark samples was performed using an accelerated solvent extraction device (ASE 200, Dionex) with the following conditions: acetone/hexane (1/1, v/v), 100°C, 10 MPa, static extraction time 10 min. The extracts were concentrated to 1 ml and subjected to a florisil clean-up. For the analysis a 30m x 0.32mm I.D. HP5 column was used. The samples were injected in the splitless mode at 220°C and the temperature programme was as follows: initial temperature 50°C (held for 8 min), increased at 6°C/min to 250°C and held at the final temperature for 5 min. The detector temperature was 300°C. The carrier gas was hydrogen, and the make-up gas ECD nitrogen.

2.3. Statistical and computer-aided data analysis

Maps of airborne pollutants in pine barks were calculated for the Nature Park Dübener Heide area using the surface mapping system Surfer ver. 6.0 (Golden Software Inc., Golden, Colorado, USA). The contour lines were interpolated by the simple Kriging method. The data were subjected to analysis of statistical parameters by using the statistical package SPSSPC+4.0 (SPSS Inc. Chicago, USA).

3. RESULTS AND DISCUSSION

3.1. Characteristics of contaminant accumulation in pine barks

Deposition from the atmosphere forms the input of airborne pollutants to the pine stand (Fig.2). Deposition can be divided into dry deposition and wet deposition. In pine forests, part of the precipitation (wet deposition) falls through the canopy without being intercepted, while another part is intercepted. The sum of both parts is called the crown throughfall. The part running down the tree trunk is called stemflow. The stem deposition as well as parts of the dry deposition and throughfall forms the bark deposition. According to element profiles of sulphur, iron and calcium in a piece of bark as shown in Fig.3, the accumulation process of airborne substances takes place on the outer porous layer of bark surface. For all three elements, a significant concentration gradient is observed between 0.5 and 1.5 mm bark depth, with only low concentration levels at deeper bark layers [10]. It follows that sampling of the outer 2 mm bark will be sufficient for the analysis of pollutants taken up from the air.

The accumulation process of airborne substances is closed with the regeneration of the bark surface (repulsion). After ca. two years, the external bark sheet is rejected, and a new bark layer is formed by sheets (approximately 1-2 mm thick) growing from inside. Correspondingly, a new accumulation process starts after each regeneration of the external bark layer. Due to the small size of the accumulation layer of the bark, only limited time will be necessary to reach equilibrium between the accumulated compound contents and the part of crown throughfall running down the tree trunk.

Table I shows minimum and maximum concentrations (mg g^{-1} d.w.) of various inorganic and organic substances in pine barks from differently polluted areas in Northern, Central and Eastern Europe. The highest concentrations were determined for sulphate, calcium, iron and ammonium. Organic substances are found in relatively low concentrations. Here, the bioindication index (maximal content/minimal content) ranges from 15 to 50. Much larger differences up to bioindication indexes of 1900 are found for inorganic pollutants such as sulphate (1900) and aluminium (1500) as well as mercury (1200). These concentration ranges indicate, that differences in airborne pollution can be reasonably well reflected by corresponding differences in accumulated contamination loads in the barks of pine stands.

In Table II are summarized the determined mean concentrations of selected elements and compounds in bark samples, which were collected in various European background and impact areas. All concentration values show a clear differentiation between background areas (National Park Jostedalsbreen, Syktywkar) and impact areas (Bialowieska, Neuglobsow, Rösa). For example, the sulphur values of Jostedalsbreen (Norway) and Syktywkar (Russia) are 200-10 times lower than those in the impact areas in East Germany (e.g. Neuglobsow, Rösa). A similar trend is found for the concentrations of all trace elements, e.g. cadmium that increases from 0.2 ppm in the background area of Norway and Russia to 20.9 ppm in Rösa. High concentrations of benzo(a)pyrene and a-hexachlorocyclohexane were measured in pine barks from Rösa. Pine barks reflect the atmospheric depositions of nutrient and heavy elements as well as polycyclic aromatic hydrocarbons and organochlorine compounds. The results are in agreement with findings of

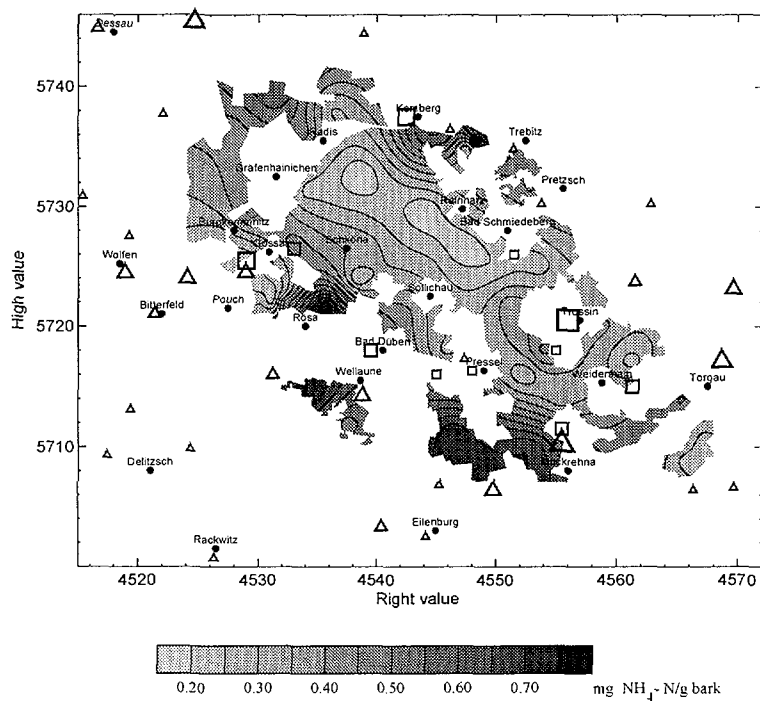


Fig.5a Spatial distribution of sulphate sulphur in pine barks from site Nature Park Dübener Heide (2.5 x 2.5 km grid of 56 test sites in Gauss-Krüger coordinates) in 1994 on the basis of mix samples. The open triangles represent locations of industry and power plants and yearly mean Deposition of sulphur ($SO_2-S + SO_3-S$) in tonnes (10-50, 50-100, 100-250, 250-1000, 1000-20000).

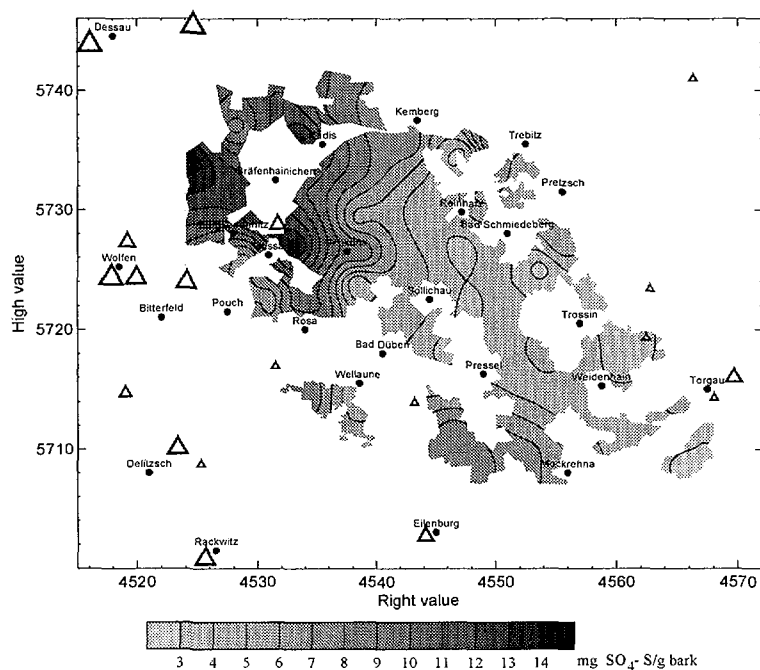


Fig.5b Spatial distribution of ammonium nitrogen in pine barks from site Nature Park Dübener Heide (2.5 x 2.5 km grid of 56 test sites in Gauss-Krüger coordinates) in 1994 on the basis of mix samples. The open triangles represent locations of industry and power plants with a yearly mean Deposition of nitrogen ($NH_4-N + NO_x-N$) in tonnes (10-50, 50-100, 100-250, 250-1000, 1000-20000). The open squares represents locations of agricultural sources with a yearly mean Deposition of nitrogen (liquid manure) in tonnes (16-40, 40-80, 80-120, > 120).

Poikolainen [11]. The raw concentrations of several deposited elements and compounds in pine bark of background areas were lowly variable and allow a reliable assessment of baseline concentrations.

3.2. Temporal variations

In Fig.4, seasonal variations are shown for sulphate sulphur, nitrate nitrogen, calcium, lead, benzo(a)pyrene and a-hexachlorocyclohexane. The data are based on bark samples collected from five low and five high polluted sites in the surroundings of Neuglobsow near lake Stechlin in the north of Berlin as well as in the surroundings of Rösa in the Dübener Heide. In comparison to the reference area Neuglobsow, bark samples from the test site Rösa indicate significantly higher depositions of airborne pollutants. The concentrations of inorganic and organic substances in barks reflect substantial infrastructural changes in former Eastern Germany since 1990: Both sulphur dioxide emissions and alkaline fly dust have been reduced significantly as compared to former times in the industrial region around the cities Leipzig, Halle, and Bitterfeld [12]. Consequently, there is a particular decrease of the concentrations of sulphate sulphur and calcium in pine barks at the site Rösa.

Similarly, the decrease of nitrate nitrogen in pine barks at both sites reflects an overall reduction of nitrogen emissions in this region. The recent increase of nitrate nitrogen concentrations in barks since 1995 can be traced back to the fact that NO_x losses due to reduced coal combustion are balanced by an increase of automobile traffic in both areas. The latter can also be seen by temporal variations of airborne lead and benzo(a)pyrene.

A further interesting fact is the general decrease of a-hexachlorocyclohexane (a-HCH) concentrations in pine barks in these areas. The semivolatile organic compound a-HCH is a waste product of the production of the insecticide lindane (g-hexachlorocyclohexane), which was stopped in the 1980s in former Eastern Germany. It is thus likely that the formerly increased a-HCH contents in barks of pine stands were due to evaporation from regional sources associated with the lindane production.

3.3. Spatial patterns

In the pine stands of the Nature Park Dübener Heide, spatial patterns of sulphate sulphur and ammonium nitrogen are studied using pine barks at 53 test sites, which were selected using statistical criteria to cover an area of 20 * 30 km in a systematic way. Application of the Kriging method for linear interpolation leads to the contour maps of Fig. 4a and b, showing the spatial patterns of $\text{SO}_4\text{-S}$ and $\text{NH}_4\text{-N}$ in pine stands of the Nature Park Dübener Heide.

As can be seen from Fig.5a, high contents of $\text{SO}_4\text{-S}$ in pine barks are mainly found in the north-west around Gräfenhainichen. Here, mean concentrations of sulphate sulphur ($14 \text{ mg SO}_4\text{-S g}^{-1} \text{ bark}$) are substantially higher than in the periphery with typical values of $3\text{-}4 \text{ mg SO}_4\text{-S g}^{-1} \text{ bark}$. Analysis of the local infrastructure reveals combustion processes, e.g. from brown coal power plants and private house heating, as major emission sources. Furthermore, the data in Fig.4a show a general decrease in $\text{SO}_4\text{-S}$ from west to east. Additional hot spots are given in the north and south of the Nature Park Dübener Heide as well as in the industrial area from Bitterfeld and Leipzig.

Fig.5b shows corresponding spatial patterns of $\text{NH}_4\text{-N}$. The overall pictures indicate significant differences in the local deposition structure. In contrast to $\text{SO}_4\text{-S}$ with one major emission area, nitrogen emission is apparently caused by a number of agricultural sources mainly in the periphery of the Nature Park Dübener Heide. The NH_3 deposition is likely to result mainly from livestock management and partially also from fertilizer application. This would be in agreement with an earlier suggestion, that the contribution from agriculture to total NH_3 emission in East Germany amounts to more than 90% [13].

4. SUMMARY AND CONCLUSIONS

The results show how pine tree barks can be used as a biomonitoring tool to indicate depositions of airborne pollutants in pine stands. In particular, this bark technique offers a new way to scale up measuring results from individual sites to the area in the field. Barks of pine trees appear to be well suited for monitoring of various inorganic and organic airborne pollutants, which are deposited in pine stands. Pine barks are inert, show good accumulation properties in relatively short times and are easy to handle.

Furthermore, the bark method offers a simple way to study temporal and spatial patterns of airborne pollutants on regional and supra-regional scales. In the Nature Park Dübener Heide, the results of sulphate sulphur and ammonium nitrogen reflect inputs from power plants, house heating and agriculture. It is suggested that on the basis of a statistically selected network of measuring sites, analysis of contaminant profiles in pine barks yields useful information for the evaluation of possible ecotoxicological effects of airborne pollutants on forest ecosystems.

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