

## Suitability of pine bark to evaluate pollution caused by cement-lime dust

A. ŚWIERCZ

*Institute of Geography, Pedagogical Academy, Kielce, Poland*

**ABSTRACT:** The aim of this paper is to show the application of pine bark to indicate the level of air contamination by cement-lime dust and to determine the impact range of cement plants. The pine bark was analyzed in the forested area around three cement plants in the Świętokrzyski administrative district (South of Poland). The test results were compared with the results gained from the controlled forested areas, free from alkali contamination. The strongly alkali areas show high  $\text{pH}_{\text{H}_2\text{O}}$  of bark in the range of 7.2–8.5 and low coefficient of change  $\nu\% = 2.2$ . The pine bark values of  $\text{pH}_{\text{H}_2\text{O}}$  in the alkali areas are on average 2.5 times as high as those achieved in the controlled area (natural pH of bark shows the range of 2.8–3.5). On the basis of the measurements of  $\text{pH}_{\text{H}_2\text{O}}$  there are five alkali-forested spheres determined. The existence of the forest spheres confirms the variable mineral composition of the bark, and first of all the variable content of calcium, magnesium, potassium, aluminium, manganese, zinc and iron as a function of the distance from the emitter and real dust fall.

**Keywords:** alkali dust; pine bark; pH

Rock raw material exploitation has been of long tradition in Poland. However, due to alkalization, the intensification of changes that began more than 30 years ago should be associated with the localization of cement plants, lime plants and aggregate plants in this area. Cement dust entering the soil in large quantities causes increasing of  $\text{CaCO}_3$  concentration in the horizons, which evokes a series of the consequences in phytocenoses (BOROWIEC, ZABŁOCKI 1983; DALE, BALL 1991; BRÓŻ et al. 1992; KREUTZER 1995; ŚWIERCZ 1997). Especially susceptible to slight changes are the oligotrophic gatherings of pine forests. The range of alkali deposit impact depends on the source and type of emission, the distance from the emitters, the orography of the area, frequency and direction of winds, among others (DAMME, ERNST 1989; SPOREK 1995; ŚWIERCZ 1997).

The aim of this paper is to:

- check the suitability of pine bark to indicate the degree of air pollution caused by cement-lime dusts,

- define the range of a cement plant impact in connection with the results obtained by SPOREK (1995) in the Opole forests.

Pine bark was analyzed in the forests located at three cement plants in the Świętokrzyski province (South Poland).

### MATERIAL AND METHODS

The testing data were collected from the pine forests located in the Świętokrzyski province. The forested areas tested are located in proximity of three cement plants and the control one in Wymysłów, located outside the impact of alkali dust emissions.

In total 310 bark samples were collected from the trees at the breast height diameter.

The bark in question was removed by means of a bark knife. The pine bark was dried in room temperature, then it was rinsed with water and dried again (approximately 40°C) for 24 hours. The dried material was milled into dust powder in a Fritsch mill.

From each sample 4 g of powdered bark were weighed and immersed in distilled water at the ratio of 1:10. After 48 hours the content of dilutions was mixed and  $\text{pH}_{\text{H}_2\text{O}}$  determined by means of digital parameter.

The selected pine samples (55) were combusted in the electrical furnace at the temperature of approximately 480°C, and then after opening in  $\text{HCl-HNO}_3$  (at the ratio of 3:1), metallic elements' content was determined by ICP-AES method with the use of Jobin-Yvon spectrometer, model JY 70 PLUS. The dependency between  $\text{pH}_{\text{H}_2\text{O}}$  of the bark and the distance from the source of emission was analyzed by means of regression and linear correlation method. The results of the tests were compared with the results achieved in the control forested area free from alkali pollution.

## RESULTS AND DISCUSSION

The control area was located in the region of the National Park at the settlement of Wymysłów. There are pine forests *As. Peucedano-Pinetum* (W. Mat. 1962) and *Leucobryo-Pinetum* (W. Mat. 1962) with pine trees at the age of 60–80, on rusty and podzolized soils (Systematics of Polish soils 1989). They are characterized by good healthy condition and proper growth without any clear anthropogenic impact. The pine bark collected from 40 trees is characterized by natural  $\text{pH}_{\text{H}_2\text{O}}$  in the range of 2.81–3.47 and a low coefficient of variation  $V = 4.06\%$  (Table 1). The separation of the tested characteristics amounts at 0.66 pH, the measurement average 3.29  $\text{pH}_{\text{H}_2\text{O}}$  while the modal amounts at 3.21. Such values are typical of the pine bark col-

lected from the areas free from industrial emissions (BIAŁY 1983; SPOREK 1995; MIGASZEWSKI 2000; MIGASZEWSKI et al. 2001).

The alkalized areas were located around three cement plants: Sitkówka, Małogoszcz, Ożarów. Pine forests growing in the areas surrounding the cement plant show bad healthy condition. Although the pine trees subject to analysis are at the same age as those controlled ones they show slight annual growth and considerable tree top defoliation. The pine bark was collected from the total 270 trees growing within 300 m to 6 km from the cement plant (90 samples each in the area close to the cement plants located at Sitkówka, Małogoszcz and Ożarów).

The strongly alkalized areas are characterized by high  $\text{pH}_{\text{H}_2\text{O}}$  bark in the range of 6.53–8.5 (in the I and II spheres of the most intensified impact of the cement plant up to 1.5 km) and an extremely low coefficient of variation from  $V = 2.2\%$  to  $3.01\%$  (Table 1). The distribution of  $\text{pH}_{\text{H}_2\text{O}}$  bark measurements is dextrorotary and shows that the measured value of 53% tested samples is within the range of 6.6–8.5 (Fig. 1), and the further 35% samples are within the range of 5.2–6.5  $\text{pH}_{\text{H}_2\text{O}}$  value. On this basis it is possible to draw conclusion about the transformation of the investigated forest ecosystems.

The fall of cement-lime dusts lowers with a growing distance from the pollution emitter, which is confirmed by the changed values of  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark (Fig. 2).

The highest values of  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark are shown by the forests located at the cement plant at Sitkówka, which is confirmed by the highest emission among all three cement plants (Raport 2001). The stated  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark in the alkalized areas

Table 1. Statistic variation of  $\text{pH}_{\text{H}_2\text{O}}$  of bark at the tested areas

	Area I	Area II	Area III	Area IV	Area V	Number of sample
Locality	$\text{pH}_{\text{H}_2\text{O}}$					
	pH: min.–max.					
	Mean (x)/ standard deviation (s)/variability coefficient (V%)					
Sitkówka	7.91–8.51	6.72–7.14	5.52–6.43	4.31–4.90	3.54–3.90	90
	8.12/0.18/2.22	7.03/0.19/2.71	6.31/0.31/4.89	4.71/0.18/3.83	3.59/0.17/4.72	
Ożarów	7.32–8.21	6.63–7.04	5.32–6.12	4.11–4.70	3.2–3.7	90
	7.92/0.19/2.41	6.82/0.21/3.01	6.03/0.28/4.69	4.4/0.19/4.31	3.38/0.18/4.71	
Małogoszcz	7.23–7.91	6.53–6.81	5.04–6.03	4.03–4.51	3.10–3.45	90
	7.51/0.19/2.53	6.62/0.18/2.72	5.20/0.32/6.15	4.13/0.18/4.39	3.38/0.16/4.71	
Control plot	–	–	–	–	2.81–3.47	40
Wymysłów					3.21/0.13/4.06	

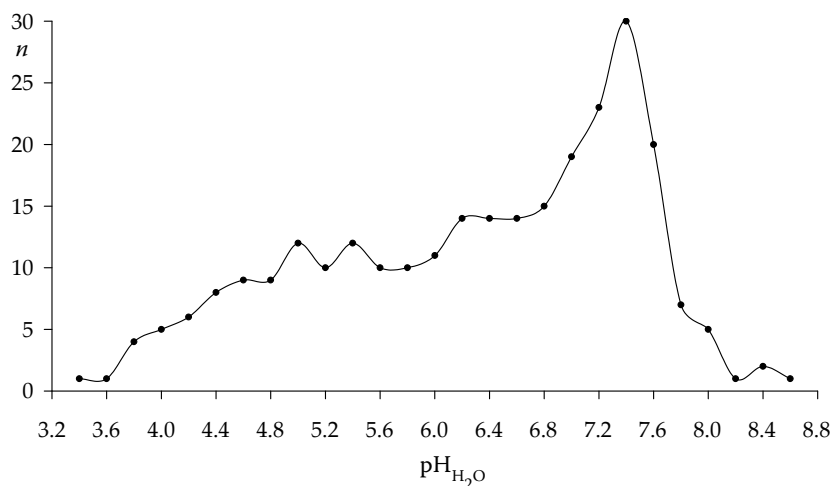


Fig. 1. Distribution of the number of pH measurements of bark at the alkalized areas at the distance to 6 km from the emitters

are 2.5 higher (in logarithmical scale) on average in comparison to the values achieved on the control area.

The values of metallic elements content in the samples of pine bark collected from the alkalized areas show considerable differences between the industrial alkalized areas and the control ones (Table 2).

The content of calcium in pine bark at the alkalized settlements is approximately 10 times higher and it ranges from 21,000 to 51,000 mg/kg at the coefficient of variation of  $V = 27.6\%$ , whereas in the control areas it ranges from 2,400 to 4,900 mg/kg, at the coefficient of variation of 24.5%. Potassium content is within the range of 112–1,500 mg/kg at the alkalized areas (at  $V = 62.3\%$ ), to 30–72 mg/kg at the compared ones ( $V = 28.2\%$ ). Magnesium content in the alkalized pine bark is approximately 10 times higher and it ranges from 620 to 913 mg/kg, and it varies at such a low coefficient of variation 8.9% (Table 2). Similarly the higher values were noticed

in case of the other metallic elements except aluminium (Table 2), the content of which was slightly lower and it ranged from 100 to 480 mg/kg (at  $V = 46.8\%$ ). The higher values of the standard deviation coefficient (s) and those of the coefficient of variation at the alkalized areas show higher distribution and diversification of results as well as lower stability of the content of the tested elements.

Pine needles are commonly used as a good anthropogenic indicator of air pollution (MOLSKI et al. 1983; DMUCHOWSKI, BYTNEROWICZ 1995; MANNINEN, HUTTUNEN 1995), whereas pine bark was mentioned as a pollution bio-indicator of the air by sour compounds, mainly sulphur and nitrogen (GRODZIŃSKA 1993; MIGASZEWSKI 2000). It turned out to be a good indicator of air pollution by cement-lime dust, which was shown by SPOREK's studies (1995). The conducted research in the conditions of the considerably lowered alkali emission confirms the suitability of pine bark to define the borderlines of the cement plants' impact.

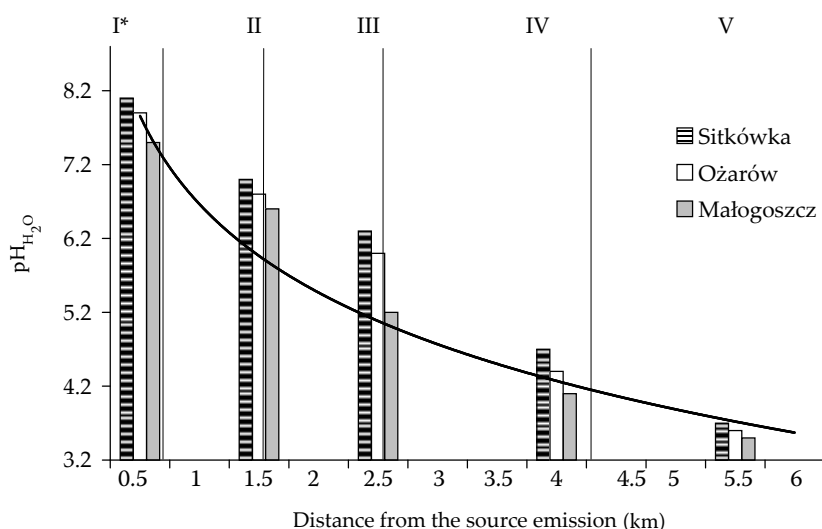


Fig. 2. Change of modal value of pH<sub>H<sub>2</sub>O</sub> of bark at the three alkalized stands close to the cement plants at Sitkówka, Ożarów, Małogoszcz

\*explain: ranges of intensification of the cement plant impact: five (I–V) spheres of alkalization of the forested areas

Table 2. Content and variation of metallic elements in the bark samples of the investigated areas

Locality, Number of sample ( <i>n</i> )	Parameter	The metallic elements mg/kg DM												
		Al	Ca	Fe	K	Mg	Na	Ba	Cu	Mn	Pb	Sr	Ti	Zn
Alkalic area: Sitkówka, Ożarów, Małogoszcz <i>n</i> = 45	min.–max.	100–480	21,000–51,000	320–1,400	112–1,500	620–913	20–60	5–40	8–34	24–280	21–46	7–52	9–22	38–95
	mean	253.0	36,758.3	892.7	834.2	794.6	33.0	24.5	15.8	125.8	32.8	32.5	15.3	69.0
	standard deviation	118.4	10,139.6	390.9	520.1	70.9	15.1	13.8	8.4	95.7	7.8	18.2	4.6	20.4
	V%	46.8	27.6	43.8	62.3	8.9	45.7	56.3	52.8	76.1	23.8	56.1	29.9	29.5
Control plot Wymysłów <i>n</i> = 10	min.–max.	560–740	2,420–4,900	565–711	30–72	60–88	20–35	2–4	6–8	65–72	37–49	8–11	15–19	26–31
	mean	657.5	4,200.0	649.5	53.5	76.3	27.3	3.0	7.0	68.3	43.8	9.5	16.5	28.8
	standard deviation	71.5	1,030.6	53.5	15.1	11.1	5.4	0.7	0.7	2.6	5.0	1.1	1.7	1.9
	V%	10.9	24.5	8.2	28.2	14.6	19.7	23.6	10.1	3.8	11.4	11.8	10.1	6.7

## CONCLUSION

On the basis of fundamental  $\text{pH}_{\text{H}_2\text{O}}$  differences five alkali spheres of the forested areas can be determined:

- I sphere of extremely strong alkali influence at the distance of 0.8 km from the emitter with  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark within 7.2–8.5;
- II sphere of strong alkali influence to the distance of 1.5 km from the emitter with  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark within 6.5–7.1;
- III sphere of lowered alkali influence to the distance of 2.5 km from the emitter with  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark within 5.0–6.4;
- IV ecoton sphere to the distance of 4.5 km from the emitter with  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark within 4.0–4.9;
- V acidophilus sphere with  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark < 3.9.

This division shows the suitability of  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark as an alkali pollution bio-indicator of the forested environment (SPOREK 1995). In the conditions of dust pollution there is a shift of  $\text{pH}_{\text{H}_2\text{O}}$  of pine bark from natural acid reaction to neutral and alkaline reaction.

On the basis of the bark reaction it is possible to draw isolines of eutrophic impact in forests, which may be important to evaluate the losses caused by cement dusts and the forest environment. The existence of the forest spheres confirms the variable mineral composition of the bark, and first of all the variable content of calcium, magnesium, potassium, aluminium, manganese, zinc and iron as a function of the distance from the emitter and real dust fall.

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## Využití borové kůry pro indikaci úrovně kontaminace ovzduší cemento-vápenným prachem

A. ŚWIERCZ

*Institute of Geography, Pedagogical Academy, Kielce, Poland*

**ABSTRAKT:** Cílem práce je ukázat využití borové kůry pro indikaci úrovně kontaminace ovzduší cemento-vápenným prachem a stanovit rozsah poškození způsobený cementárnami. Borová kůra byla analyzovaná v lesích kolem cementáren na jihu Polska v okrese Świętokrzyski. Výsledky testu byly srovnány s výsledky získanými z kontrolních ploch bez kontaminace, umístěných v oblasti Národního parku u osady Wymysłów. Silně alkalické oblasti vykazovaly vyšší  $\text{pH}_{\text{H}_2\text{O}}$  v kůře v rozmezí 7,2–8,5 a nízký koeficient změny  $\nu\% = 2.2$ . Hodnoty  $\text{pH}_{\text{H}_2\text{O}}$  borové kůry jsou v průměru 2,5krát vyšší než výsledky získané z kontrolních ploch (přirozené pH kůry se pohybuje v rozmezí 2,8–3,5). Na základě měření  $\text{pH}_{\text{H}_2\text{O}}$  bylo stanoveno pět alkalicky ovlivněných lesních oblastí. Existence lesních oblastí potvrdilo proměnlivé minerální složení kůry; nejvíce proměnlivé byly obsahy vápníku, hořčíku, draslíku, hliníku, manganu, zinku a železa. Jejich obsah závisel na vzdálenosti od emitenta a prašného spadu.

**Klíčová slova:** alkalický prach; borová kůra; pH

Cílem práce je ukázat využití borové kůry pro indikaci úrovně kontaminace ovzduší cemento-vápenným prachem a stanovit rozsah poškození způsobený cementárnami. Borová kůra byla analyzovaná v lesích kolem cementáren na jihu Polska v okrese Świętokrzyski. Výsledky testu byly

srovnány s výsledky získanými z kontrolních ploch bez kontaminace, umístěných v oblasti Národního parku u osady Wymysłów. Silně alkalické oblasti vykazovaly vyšší  $\text{pH}_{\text{H}_2\text{O}}$  v kůře v rozmezí 7,2–8,5 a nízký koeficient změny  $\nu\% = 2.2$ . Hodnoty  $\text{pH}_{\text{H}_2\text{O}}$  borové kůry jsou v průměru 2,5krát vyšší než vý-

sledky získané z kontrolních ploch (přirozené pH kůry se pohybuje v rozmezí 2,8–3,5). Na základě měření  $\text{pH}_{\text{H}_2\text{O}}$  byly stanoveny pět alkalicky ovlivněných lesních oblastí:

I. oblast: extrémně silně alkalický vliv ve vzdálenosti 0,8 km od emitora s  $\text{pH}_{\text{H}_2\text{O}}$  borové kůry pohybující se v rozmezí 7,2–8,5;

II. oblast: silně ovlivněna alkalickým vlivem ve vzdálenosti 1,5 km od emitora s  $\text{pH}_{\text{H}_2\text{O}}$  kůry v rozmezí 6,5–7,1;

III. oblast: snížený alkalický vliv ve vzdálenosti 2,5 km od emitora s  $\text{pH}_{\text{H}_2\text{O}}$  kůry v rozmezí 5,0–6,4;

IV. ekotonická oblast: ve vzdálenosti 4,5 km od emitora s  $\text{pH}_{\text{H}_2\text{O}}$  kůry v rozmezí 4,0–4,9;

V. acidofilní oblast:  $\text{pH}_{\text{H}_2\text{O}}$  borové kůry < 3,9.

Existence lesních oblastí potvrdilo proměnlivé minerální složení kůry; a nejvíce proměnlivé byly obsahy vápníku, hořčíku, draslíku, hliníku, manganu, zinku a železa. Jejich obsah závisel na vzdálenosti od emitenta a prašného spadu.

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*Corresponding author:*

Dr. inż. ANNA ŚWIERCZ, Institute of Geography, Pedagogical Academy, Świętokrzyska 25, 25-406 Kielce, Poland

tel.: + 48 413 496 428, fax: + 48 223 317 524, e-mail: swierczag@poczta.onet.pl

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