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INFLUENCE OF AIR POLLUTION ON THE BARK pH-VALUES IN THE REGIONS OF ZAGREB AND SISAK

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The bark pH-values of deciduous trees were measured on the localities with different degrees of air pollution, i.e. SO_2 immission, in the regions of Zagreb and Sisak. In both cities *Quercus robur* and *Tilia cordata* were investigated, while *Acer platanoides* and *A. pseudoplatanus* were examined in Zagreb and *Tilia tomentosa, Betula pendula* and *Populus italica* only in Sisak.

Lower bark pH-values were measured on the localities with greater air pollution, i.e. SO_2 immission, and higher values were shown by specimens of the same species growing on comparatively less polluted localities.

These data are in accordance with those obtained in some other areas of Europe (Sweden, Poland, FR Germany), confirming that bark pH-values could be used as indicators of SO_2 immission.

Introduction

Investigations of bark pH-values in some areas of Europe, in Sweden (Staxäng 1969), Poland (Grodzińska 1971) and Germany (Lötschert and Köhm 1973) have shown that an increase of air pollution, particularly in SO_2 concentration, decreases the bark pH-values, in comparison to the specimens of the same species and similar age growing in more natural habitats with clean or less polluted air. So, the bark pH-value could be used as an air pollution indicator. That was the reason of our investigations in the regions of Zagreb and Sisak in Croatia.

Area and Subjects of Investigations

As mentioned above, investigations were made in the region of Sisak in 1982 and in the region of Zagreb in 1984, comparatively on following localities:

Sisak

1. Sisak — Ironworks, Rafinery (the most polluted part of Sisak). Distance from city center about 4 km.
2. City center (the most severe pollutants are house heating and motor vehicles).
3. Close surroundings, about 1,5 km northwest of city center, along the Sisak—Zagreb road (the most severe pollutants are motor vehicles railway engines and house heating).
4. Village of Žabno at the Odra river, 3.5 km northwest of city center (sources of pollution are mostly house heating, and to a lesser extent motor vehicles).
5. Surroundings of the village of Stari Brod, 17 km of Sisak, where the vegetation grows in more natural conditions, without significant, direct air pollution.

Zagreb

1. City center (Marulić Square — Zrinjevac, sources of pollution are primarily motor vehicles, house heating, railway engines owing to the vicinity of the railroad station).
2. Lenjin Square, about 2 km east of the previous locality (the same sources of pollution as on the previous locality).
3. Maksimir park-forest on the northeastern outskirts of the town (sources of pollution are mostly motor vehicles driving along the edge of Maksimir, as well as house heating in the neighbouring settlements at the margin of the wood).
4. Jarun, near the lake, northeastern outskirts of the town.
5. Sljeme, top of Medvednica Mountain (Zagrebačka gora) at the altitude of about 960 m a.s. (the zone of beech and beech-fir woods), the least polluted area.

The tree species present on the locality with five or more specimens (exceptionally 4 or 2) were involved in experiments on the localities in Zagreb and Sisak. In addition, the similarity of age and thickness for specimens of the same species on the locality were taken into account. Unfortunately, it was not possible to achieve this completely, but trees with a diameter of less than 20 cm were not taken into experiment. Considering the diameter of chosen trunks, the situation was better in Sisak than in Zagreb.

Results for Sisak refer to 5 species with a total of 194 investigated tree specimens. Four species with a total of 65 tree specimens were investigated in Zagreb. The number of trees for each species and locality is given in Tables 3 and 4.

Seven species of deciduous trees were investigated. In both regions (Sisak and Zagreb) these involved the species *Quercus robur* and *Tilia cordata*, the species *Betula pendula*, *Tilia tomentosa* and *Populus nigra* cv. *italica* were examined only in Sisak, while *Acer pseudoplatanus* and *A. platanoides* were investigated only in Zagreb.

Methods

Collecting and preparation of bark samples and pH determination were made according to the method by Lötschert and Köhm (1973) with slight modifications. The bark samples of chosen tree specimens were collected at the height of 130—140 cm above the ground surface, on an area of 25 sq. cm, 3 mm thick. They were dried on air and then crumbled and suspended in 20 ml of distilled water. After 48 hours the suspension was agitated for 8 hours and then the pH-value was measured in suspension by a pH-meter with glass electrode.

SO_2 Concentration in the Air

To offer an easier and more detailed interpretation of results obtained by bark pH-measurements on the various localities, it would be useful to know the air pollution, i.e. SO_2 immission on each locality.

So far, unfortunately, few data have been available for some localities only. Here we give some data for some localities in Sisak and Zagreb, showing the air pollution on the localities in the period of investigation; these data have not been published yet. The data for Sisak were obtained from a manuscript by Borić et al. (1982), and for Zagreb from the Hydrometeorological Department of the S.R. of Croatia, which are gratefully acknowledged.

1. Sisak

The data about SO_2 concentrations in the period 1975—1981 in the city center and on the locality near the Ironworks according to Borić et al. (1982) are given in Tab. 1.

Table 1. SO_2 concentration in the air in Sisak ($\mu g/m^3$)

Year	Mean yearly concentration		Maximum yearly concentration	
	Ironworks	Center	Ironworks	Center
1975/76	29	40	174	167
1976/77	27	28	136	104
1977/78	55	41	231	147
1978/79	60	37	470	181
1979/80	73	40	332	324
1980/81	54	28	204	132

It is obvious that the greatest difference in the mean yearly amounts was noted in 1979/1980, when the mean SO_2 concentration was 40 $\mu g/m^3$ in the city center, and as high as 73 $\mu g/m^3$ near the Ironworks. In the same period there were some slight differences in the maximum concetrations. The greatest difference in the maximum concentrations was noted in 1978/79, when 470 $\mu g/m^3$ was recorded at Ironworks and »only« 181 $\mu g/m^3$ in the city center.

According to data in Table it is obvious that air pollution was generally greater at Ironworks than in the city center, where the SO_2 immission was lower.

There were no data about the SO_2 immissions on other localities in the surroundings of Sisak where the samples were taken. Thus, we can conclude about the air pollution indirectly, according to bark pH-values.

2. Zagreb

The data about SO_2 concentration in Zagreb concern a period of five years and three localities: near the Cathedral, at Grič and in Maksimir, including monthly mean and maximum concentrations. On the basis of these data we calculated the mean yearly concentrations (Tab. 2). In addition, maximum yearly concentrations are given in the Table with the month (in brackets) shown when maximum was reached.

Table 2. SO_2 concentration in the air in Zagreb ($\mu g/m^3$)

Year	Mean yearly concentration			Maximum yearly concentration		
	Cathedral	Grič	Maksimir	Cathedral	Grič	Maksimir
1983	59.1	32.4	20.3	319 (II)[1]	254 (XI)	131 (II)
1984	41.0	20.8	10.8	314 (I)	335 (I)	131 (I)
1985	16.6	6.8	17.0	202 (II)[2]	171 (I)	201 (I)
1986	19.8	16.6	14.5	113 (XII)	141 (I)	95 (I)
1987	16.6	16.3	15.7	102 (I)	203 (I)	163 (I)

[1] In brackets the month when maximum was measured
[2] No data available for January

SO_2 concentration was remarkably higher at the Cathedral and at Grič (localities the closest to ours in the city center, Marulić Square — Zrinjevac, where the samples were collected) than in Maksimir, particularly in 1983 and 1984. It is significant that those differences decreased later on. In our opinion this could be connected with progressive building in the eastern part of Zagreb (area of Maksimir), as well as with some efforts in the city center, causing a decrease in SO_2 (use of gas, less dense traffic etc.).

For a better presentation of differences in SO_2 concentration on three localities in Zagreb in 1984 (when bark pH-values were measured) the comparative graphic presentation of mean monthly concentrations for localities at the Cathedral, at Grič and Maksimir is shown in Fig. 1. The greatest differences were in winter period, when there were also the highest concentrations, while in summer differences disappeared, namely SO_2 concentration decreased on three localities compared.

Results and Discussion

Results of measurements of bark pH-values on five localities in Sisak and its surroundings are given in Fig. 2 and Tab. 3. Table 4 shows the results for Zagreb and Medvednica Mountain.

The lowest bark pH-values for each investigated species were noted in Sisak, at Ironworks, where air pollution was greatest, i.e. SO_2 immission. The highest bark pH-values were noted in Stari Brod, where tree grow in more natural conditions with clean (or cleaner) air (Fig. 2, Tab. 3).

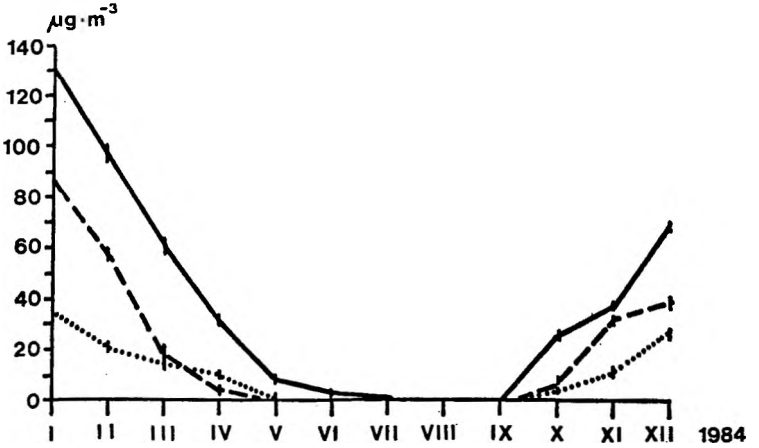

Fig. 1. Mean SO_2 concentration ($\mu g \cdot m^{-3}$) in the air on three localities in Zagreb: Cathedral (——), Grič (- - - -) and Maksimir (. . . . . .).

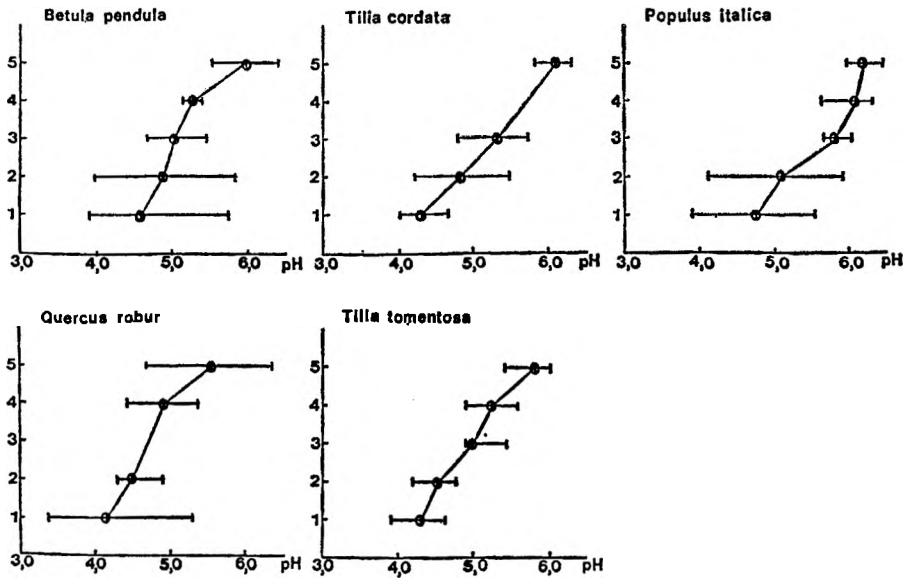

Fig. 2. Bark pH-values (mean, minimum and maximum) on five localities in the region of Sisak (ordinate): 1. Sisak Ironworks, 2. Sisak center, 3. Sisak Suburbs-area, 4. Žabno, 5. Stari Brod (»clean area«).

Table 3. Mean bark pH-values in the region of Sisak

Locality	Quercus robur	Tilia tomentosa	Betula pendula	Tilia cordata	Populus nigra cv. italica
1. Ironworks	4.12 ± 0.58 (12)	4.30 ± 0.23 (12)	4.59 ± 0.65 (12)	4.32 ± 0.53 (5)	4.75 ± 0.53 (12)
2. Sisak—Center	4.46 ± 0.25 (5)	4.53 ± 0.19 (12)	4.86 ± 0.56 (12)	4.82 ± 0.45 (5)	5.09 ± 0.64 (12)
3. Surroundings	—	4.95 ± 0.20 (10)	5.05 ± 0.32 (7)	5.31 ± 0.32 (5)	5.80 ± 0.13 (8)
4. Žabno	4.87 ± 0.34 (10)	5.24 ± 0.24 (7)	5.27 ± 0.14 (3)	—	6.08 ± 0.23 (7)
5. Stari Brod	5.53 ± 0.58 (12)	5.80 ± 0.21 (6)	5.98 ± 0.30 (6)	6.07 ± 0.25 (5)	6.17 ± 0.18 (7)

(number of trees)

Analogous results were obtained in Zagreb (Tab. 4). In comparison with other localities, the lowest bark pH-values were measured in the city center where the air pollution was the greatest. A particular differences, relating to the localities of the city center and Medvednica Mountain, were shown by the species *Acer platanoides*. Its bark pH-value was by 1.5 pH unit higher on Medvednica Mountain than in the city center (Tab. 4). The bark pH-values of *Acer pseudoplatanus* differed much less on the same localities.

Table 4. Mean bark pH-values in the region of Zagreb

Locality	Quercus robur	Tilia cordata	Acer pseudoplatanus	Acer platanoides
1. Center	3.37 ± 0.17 (8)	3.47 ± 0.08 (2)	4.33 ± 0.32 (8)	3.93 ± 0.24 (9)
2. Lenjin Square	3.39 ± 0.18 (4)	3.96 ± 0.24 (5)	—	4.27 ± 0.29 (4)
3. Maksimir	3.51 ± 0.27 (5)	4.03 ± 0.15 (5)	—	—
4. Jarun	4.23 ± 0.18 (5)	—	—	—
5. Sljeme	—	—	4.49 ± 0.29 (5)	5.41 ± 0.33 (5)

(number of trees)

It is obvious that the relations refering to pH-values measured in Zagreb and Sisak coincide with the above cited investigations in other parts of Europe (Staxäng 1969, Grodzińska 1971, Lötschert and Köhm 1973), although the pH-values were not the same.

Table 5 shows comparatively the minimum-maximum span of the bark pH-values for the species *Quercus robur, Tilia cordata, Betula pendula* and *Acer platanoides* in Sisak, Zagreb and Stockholm, and Table 6 gives mean pH-values for *Quercus robur, Tilia cordata* and *Acer platanoides* in Sisak and Zagreb as well as in Cracow and Białowieża Forest in Poland and Frankfurt /a.M. in FR Germany. In both Tables the bark pH-values in the city center are listed in column *a*, the pH-values in the surroundings in column *b*. In all the compared areas the bark pH-value was lower (more acid) in city centers, where the SO_2 immission was greater, than on comparatively »clean« or less polluted localities.

However, there were significantly higher bark pH-values in Sisak in comparison with Stockholm (Tab. 5) for all tree species which we could compare, considering the available data. Thus, we conclude that the air was more polluted in the center of Stockholm (»lichen desert«, Sky 1968) than in the city center of Zagreb or even more than in the center of Sisak. However, it should be emphasized that in Zagreb city center there was a »lichen desert« 35 years ago (Barbalić 1953, Gračanin and Ilijanić 1977). It would be interesting to establish the share of epixylous lichen flora on the same localities again today, and compare it with the previous data.

Considering the bark pH-values on »clean« localities (*b* column in Tab. 5) results for Zagreb and Stockholm coincide to a great extent. The pH-values for Sisak-Stari Brod in the surroundings are much higher for all tree species compared, the bark is less acid, which suggest less polluted air.

Table 5. Comparative review of bark pH-values in the regions of Sisak, Zagreb and Stockholm

Territory	Quercus robur		Tilia cordata		Betula pendula		Acer platanoides	
	a	b	a	b	a	b	a	b
Sisak[1]	4.27—4.87	4.65—6.32	4.23—5.47	5.80—6.30	3.95—5.82	5.52—6.40	—	—
Zagreb[2]	3.17—3.69	3.98—4.45	3.39—3.55	3.75—4.21	—	—	3.61—4.45	5.10—6.00
Stockholm[3]	2.40—2.80	3.80—4.50	2.40—2.90	4.10—4.70	2.70—4.10	3.30—4.50	2.90—3.70	5.10—6.20

1 a = Sisak center
b = Stari Brod (17 km west of Sisak)
2 a = Zagreb center (Marulić Square and Zrinjevac)
b = Jarun (*Quercus robur*), Maksimir Forest (*Tilia cordata*), Sljeme-Medvednica Mountain (*Acer platanoides*)
3 a = Stockholm center (»lichen desert«)
b = Surroundings of Stockholm (agricultural area)
note: values for birch in Stockholm refer to both *Betula pendula* and *Betula pubescens* (Skye, 1968)

Analogous results are visible in Tab. 6 with data of mean bark pH-values for species *Quercus robur, Tilia cordata* and *Acer platanoides* given comparatively for our regions (Sisak, Zagreb) and for Cracow, Białowieża Forest in Poland and Frankfurt in FR Germany. In the centers of all the above mentioned cities the bark gave a more acid reaction than in the surroundings, where the air is clean or less polluted. The highest values were found in the region of Sisak, both in the city center and the surroundings.

Table 6. Comparative survey of mean bark pH-values in some parts of Europe

Area	Quercus robur		Tilia cordata		Acer platanoides	
	a	b	a	b	a	b
Sisak	4.46	5.53[1]	4.82	6.07[1]	—	—
Zagreb	3.37	4.23[2]	3.47	4.03[3]	3.93	5.41
Krakov[+]	3.36	3.79[4]	3.76	4.14[4]	—	—
Bialowieża Forest[+]	—	3.86	—	4.20	—	—
Frankfurt a/M[++]	—	—	—	—	3.42	4.35[5]

[+] Grodzinska (1973)
[++] Lötschert und Köhm (1973)

a = city center (polluted area)
b = surroundings (comparatively »clean« area): 1 = Stari Brod (surroundings of Sisak)
2 = Jarun (outskirts of Zagreb — at the lake)
3. Maksimir Forest (northeastern outskirts of Zagreb)
4 = Krakow (Niepołomice Forest — surroundings, east of Cracow)
5 = Falkenstein (surroundings of Frankfurt)

Mean pH-values for *Quercus robur* were nearly identical (3.37 : 3.36) and negligibly different for *Tilia* in the city centers of Zagreb and Cracow. This suggests similar conditions, taking into consideration SO_2 immisson in Zagreb and Cracow, as well as cleaner atmosphere in the Sisak center and its surroundings (Stari Brod).

Acer platanoides, compared in Zagreb and Frankfurt, showed lower bark pH-values in Frankfurt (both in the center and the surroundings) than in the center of Zagreb and its surroundings (Medvednica Mountain), indicating stronger pollution in the Frankfurt region.

Data about bark pH-values in Białowieża Forest, marked by Grodzińska (1971) as »a relatively clean area in the north-eastern part of Poland«, are given in Tab. 6 (column b). Comparing it with data concerning the surroundings of Zagreb and even more of Sisak surroundings, it is obvious that mean pH-values for *Quercus robur* in Białowieża were significantly lower (5.53 : 3.86). Referring to these data, Białowieża Forest could not be considered as an area with clean air and Grodzińska (1971) related the relatively low pH-values to the influence of acid rains coming from West Europe.

Conclusions

According to the results of investigation of bark pH-values in the Zagreb and Sisak regions the conclusinos could be ordered as follows:

Bark reaction was acid for all the investigated tree species, ranging from pH 3.37 (mean values) for *Quercus robur* in Zagreb center to pH 6.17 for *Populus italica* in the surroundings of Sisak (Stari Brod).

Both in Zagreb and Sisak lower bark pH-values were noted for all the species on the localities with higher air pollution, i.e. greater SO_2 immission, than on less polluted or »clean« localities. Also, our results are in accordance with those from other European areas (Sweden, Poland, FR Germany). So one can conclude that bark pH-values can be used as indicators of SO_2 immission.

A comparison of results obtained for Zagreb and Sisak with those for Stockholm, Frankfurt and Cracow, as regards bark pH-values, has shown that there was greater air pollution, namely SO_2 immission (in the period of investigation in each of the cities) in Stockholm and Frankfurt than in Zagreb, and particularly greater than in the center of Sisak and its surroundings. The results for the center of Zagreb and Cracow coincide to a great extent.

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SAŽETAK

UTJECAJ ONEČIŠĆENOSTI ZRAKA NA pH-VRIJEDNOSTI KORE DRVEĆA NA PODRUČJU ZAGREBA I SISKA

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Istraživane su pH-vrijednosti kore drveća na području Zagreba i Siska na nekoliko lokaliteta koji se razlikuju s obzirom na onečišćenost zraka odnosno imisiju SO_2.

U pokus je uzeto 7 vrsta drveća od kojih su *Quercus robur* i *Tilia cordata* istraživane u Zagrebu i Sisku, *Acer platanoides* i *A. pseudoplatanus* samo na području Zagreba, a *Tilia tomentosa, Betula pendula* i *Populus italica* samo na području Siska.

Skupljanje i pripremanje uzoraka kore te određivanje pH-vrijednosti vršeno je po metodi kako su je opisali Lötschert i Köhm (1973) s manjim modifikacijama (v. engleski tekst).

Doneseni su i raspoloživi podaci o imisiji SO_2 na dva lokaliteta u Sisku (tab. 1) i na tri lokaliteta u Zagrebu (tab. 2, sl. 1).

U svih istraživanih vrsta kora je pokazivala kiselu reakciju, a prosječne vrijednosti izmjerene su u rasponu između pH 3,37, koliko je najniže pokazivala kora hrasta lužnjaka (*Quercus robur*) u središtu Zagreba i pH 6,17 u jablana (*Populus italica*) u okolici Siska u Starom Brodu (tab. 3 i 4, sl. 2).

I u Zagrebu i u Sisku u svake istraživane vrste najniže pH-vrijednosti (tj. najkiselija reakcija) izmjerene su na lokalitetima s većom imisijom SO_2, dok su najviše vrijednosti bile izmjerene na komparativnim (»čistim«) područjima izvan grada.

U tom su smislu naši rezultati analogni onima iz nekih drugih područja Evrope (Švedska, Poljska, SR Njemačka) gdje je utvrđena ista pravilnost (tab. 5 i 6), pa se može zaključiti da pH-vrijednosti kore drveća mogu poslužiti kao indikator imisije SO_2.

Usporedba rezultata dobivenih na području Zagreba i Siska s onima iz Stockholma, Frankfurta i Krakowa, s obzirom na pH-vrijednosti kore istovrsnog drveća, pokazuje da je imisija SO_2 (u razdoblju na koje se odnose rezultati istraživanja u svakom od navedenih gradova) bila veća u Stockholmu i Frankfurtu nego u Zagrebu i (osobito) u Sisku i okolici. Rezultati za središte Zagreba i Krakowa pokazuju veliku podudarnost.

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