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INFLUENCE OF THE COMBINATED BIOACCUMULATION OF FLUORIDE AND SULFUR ON CHLOROPHYLL CONTENT IN NEEDLES OF SELECTED TREES FROM THE AREAS OF SOUTHERN POLAND

WPŁYW ŁĄCZONEJ BIOAKUMULACJI FLUORU I SIARKI NA ZAWARTOŚĆ CHLOROFILU W IGŁACH WYBRANYCH DRZEW ROSNĄCYCH NA TERENACH POLSKI POŁUDNIOWEJ

Abstract: It was the fluorine (F), sulfur (S) and chlorophyll (Chl) content that was determined in the needles of conifer species: European spruce (*Picea abies*), Colorado spruce (*Picea pungens*), Scots pine (*Pinus silvestris* L.) and Common silver (*Abies alba*). The materials were collected in the regions located in the vicinity of steel and power engineering industry impact and in a place situated in a non-industrial area. The obtained results were analyzed from the viewpoint of the relationships between the S, F and chlorophyll content. From the findings, it appears that, accumulation of F and S in needles only in case of Scots pine has been accompanied by more evident decrease in the Chl content. In the case of remaining conifer species increased accumulation of F and S in older needles did not influence the Chl content therein.

Keywords: industrial pollution, fluorine, sulfur, chlorophyll, needles of conifer

Sulfur (S) as SO_2 and fluorine (F) usually in the form of HF or SiF_4 are one of the most important air pollutants damaging the plants. The main emission source of the industrial gases and dusts, which introduce toxic compounds of S and F to environment are cement and aluminum works, phosphate fertilizers plants, iron- and steel works and power industry [1]. Increasing concentration of S and F in the soil of agricultural regions results from application of fertilizers and plant protection substances [2].

The high concentration of S and F in the atmosphere and long duration of exposure, induce chlorosis, necrosis and growth distortion in the plants, whereas the first symptom of concentration of S and F that does not cause visible damage are photosynthesis

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processes disturbances [3, 4]. Thus, one of the manners in which it is possible to evaluate the conditions of the trees growing in a polluted environment is to analyze the changes in the chlorophyll content in the tree leaves and needles [5–7].

These studies have been aimed at determination of the relationship between chlorophyll and fluorine and sulfur concentration in needles of selected conifers exposed to fluorine and sulfur bearing gaseous emissions.

Materials and method

The needles of four conifer species growing in Poland: European spruce (*Picea abies*), Colorado spruce (*Picea pungens*), Scots pine (*Pinus sylvestris*) and Common silver (*Abies alba*) were examined. The current-year and one-year-old needles were collected between November and February in the physiological rest period, during the same season in the years 2001–2003. The samples come from Polish southern towns of Strzemieszyce, Ustroń Polana and Zebrzydowice located in areas of iron, steel and heat-power generating plants and also from Brzezna near Nowy Sącz situated in a non-industrial area. Strzemieszyce is located within a distance of 6 km from Huta Katowice (presently ArcelorMittal Steel branch of Dąbrowa Górnicza). In Ustroń Polana (situated in Beskid Śląski) the needles were torn off the tree growing on the slopes of the Czantoria Mount. The needles of the Colorado spruce come from allotment gardens and the needles of Common silver were collected only on the Czantoria Mount. The needles without visible symptoms of chlorosis and necrosis were collected at an altitude of 2.5–3 m above ground.

The uniform samples were prepared for analysis. Fluoride ion (F^-) concentration was determined potentiometrically [8], using fluoride selective electrode (Orion, USA) and sulfur (S) concentration was determined nephelometrically with $BaCl_2$ as sulfate (SO_4^{2-}), after dry ashing the needles in nickel crucible. Fresh needles were extracted with acetone for spectrophotometric determination of chlorophyll (Chl) [9].

Results and discussion

In order to evaluate the impact of F and S accumulation in the needles of the conifer species on the Chl content therein, the materials were collected in the places that were under influence of differential emission of these compounds. The average F and S content in the needle samples from all the collection sites are shown in Table 1. A significant concentration diversification was observed, both in the case of F and S, which indicates their accumulation from atmospheric air (Table 1). The highest and the lowest F contents were found in needle samples of the coniferous trees grown in Strzemieszyce (near the steel works) and in Brzezna (situated in a non-industrial area), respectively. Considerably, unexpectedly high S content in the needles coming from Brzezna may have been associated with the household combustion of high-sulfur--content coal in this area [10]. On the other hand, Innes [11] argued, that the good

nutritional status of trees may be a possible reason for the unexpectedly high sulfur content.

Table 1

Average of fluorine (F) and sulfur (S) content in the needle samples depending on the collection site

Element	Collection site			
	Strzemieszyce	Ustroń Polana	Zebrzydowice	Brzezna
F [μg g^{-1} d.m.]	15.52 ± 10.20	14.86 ± 6.51	8.99 ± 2.97	6.86 ± 1.98
S [μg g^{-1} d.m.]	1706 ± 363	1432 ± 245	1562 ± 295	1794 ± 299

In Figs. 1A, B it is shown that accumulation level of F and S depends on the needle age. The S content showed no significant decrease between current- and one-year-old needles, while the F content was increasing with the ageing of needles. The results of average F, S and Chl content in the needle samples from particular species are presented in Table 2. In all examined needles the content of F varied from 4.44 μg g^{-1} d.m. to 41.87 μg g^{-1} d.m. and the content of S was between 842 μg g^{-1} d.m. and 2552 μg g^{-1} d.m. The obtained results are similar to the results reported by other authors. The content of S obtained by Ciepał [12] was between 1400 μg g^{-1} d.m. and 1750 μg g^{-1} d.m. and by Mańkowska [13] was from 2251 μg g^{-1} d.m. to 2590 μg g^{-1} d.m. for needles of the European spruce. The lowest concentration of all the elements analyzed was found in the Scots pine needles. However, these values were higher than the values assumed as non-toxic, this is, 1300 μg g^{-1} d.m. [14, 15] and 6 μg g^{-1} d.m. [16] for S and F, respectively.

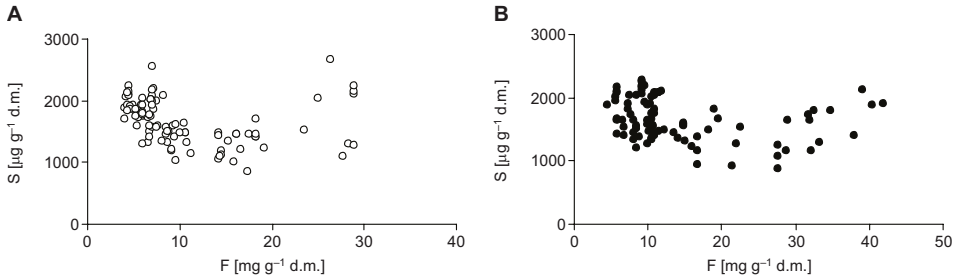

Fig. 1. Relationships between fluorine and sulfur content in (A) current-year needles and (B) one-year-old needles of the investigated conifer species from all of the collection sites. Explanation: F – fluoride; S – sulfur

The interdependency between the F, S and Chl content is depicted in Figs. 2A–C and Figs. 3A–C. From the results, it appears that accumulation of both elements in needles only in the case of Scots pine has been accompanied by more evident decrease in the Chl content. In the case of remaining conifer species increased accumulation of F and S in older needles did not cause decrease of Chl content therein.

Table 2

Fluorine (F), sulfur (S) and chlorophyll (Chl) content in needles of conifer species from all of the collection sites

Element	Age of needles	Conifer species			
		Scots pine	*European Spruce*	*Colorado Spruce*	*Common silver*
		Mean (min.–max.)			
F [μg g^{-1} d.m.]	current-year	11.66	11.02	10.62	15.92
	one-year-old	14.25	12.48	14.70	16.53
		(4.32–32.14)	(4.44–34.83)	(4.59–41.87)	(13.55–19.14)
S [μg g^{-1} d.m.]	current-year	1538	1744	1694	1675
	one-year-old	1543	1740	1556	1626
		(1171–2081)	(952–2552)	(842–2246)	(1127–2311)
Chl [μg g^{-1} d.m.]	current-year	1.44	1.74	1.54	1.82
	one-year-old	1.59	2.25	2.02	2.56
		(1.07–2.07)	(1.26–2.71)	(1.29–2.68)	(1.31–2.78)

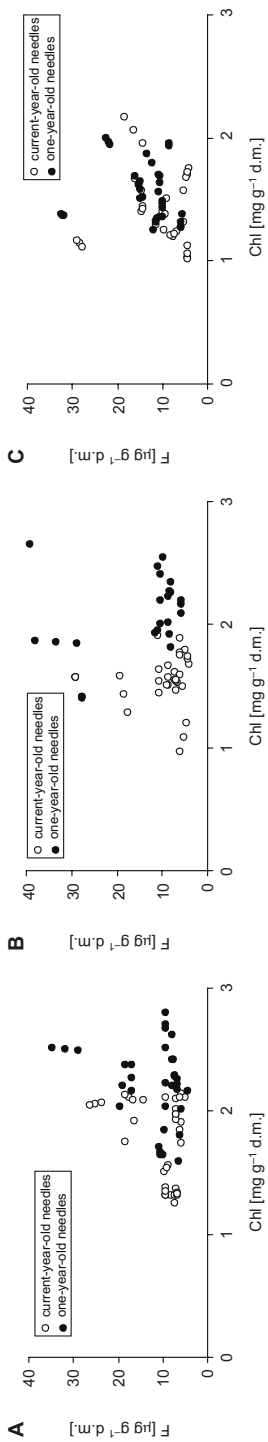

Fig. 2. Relationships between chlorophyll and fluorine contents in current- and one-year-old needles of (A) European spruce, (B) Colorado spruce and (C) Scots pine from all of the collection sites. Explanation: F – fluoride; Chl – chlorophyll

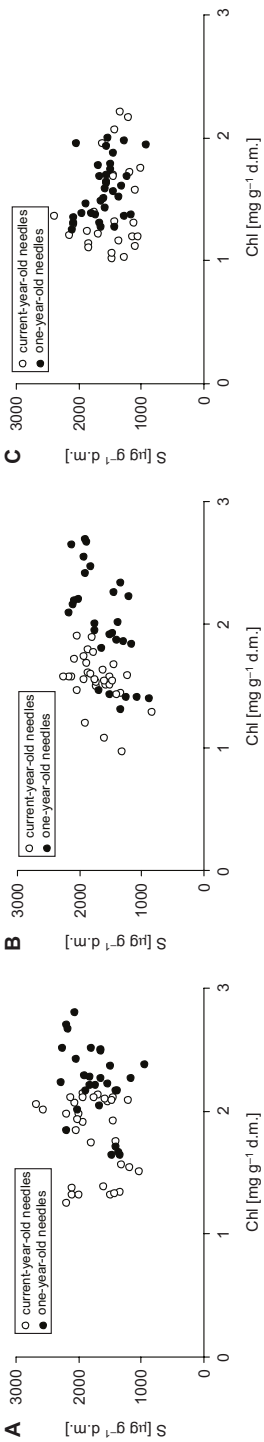

Fig. 3. Relationships between chlorophyll and sulfur contents in current- and one-year-old needles of (A) European spruce, (B) Colorado spruce and (C) Scots pine from all of the collection sites. Explanation: S – sulfur; Chl – chlorophyll

In the light of the results achieved, one may conclude that the investigated needles of coniferous trees growing in the same area are characterized by differential sensibility on the same pollution impact. These results may show that needles of Scots pine are more sensitive to F and S from atmospheric air.

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Abstrakt: Zawartość siarki (S) i fluoru (F) oraz chlorofilu (Chl) oznaczano w igłach świerka pospolitego (*Picea abies*), świerka kłującego (*Picea pungens*), sosny pospolitej (*Pinus sylvestris*) i jodły pospolitej (*Abies alba*). Materiał do badań pobierano w miejscowości Strzemieszyce, Ustroń Polana (Beskid Śląski) i Zebrzydowice (powiat cieszyński) znajdujących się w strefach oddziaływania zanieczyszczeń z ośrodków przemysłowych Polski i zanieczyszczeń transgranicznych oraz w miejscowości Brzezna położonej koło Nowego Sącza. Uzyskane wyniki analizowano z punktu widzenia zależności pomiędzy zawartością S i F i zawartością chlorofilu w igłach. Spośród badanych gatunków drzew iglastych jedynie w przypadku igieł sosny pospolitej stwierdzono zmniejszenie zawartości chlorofilu związane z akumulacją F i S.

Słowa kluczowe: zanieczyszczenia przemysłowe, fluor, siarka, chlorofil w igłach drzew