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$\delta^{34}S$ values and S concentrations in native and transplanted *Pleurozium schreberi* in a heavily industrialised area

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ABSTRACT

Sulphur is an element found in surplus in anthropogenic areas and one of the minerals responsible for the development of acid rains. The analysis of stable S isotopes provides a powerful tool for studying various aspects of the biogeochemical circulation of sulphur. $\delta^{34}S$ values and S concentrations were determined in a 90-day experiment with the native moss *Pleurozium schreberi* from rural, urban and industrial sites in Upper Silesia in southern Poland. At the same time *P. schreberi* from a control site was transplanted to the same rural, urban and industrial sites and the $\delta^{34}S$ values and S concentrations were determined in the same 90-day experiment. ^{34}S enrichment (up to 4.7‰) in the mosses tested indicates that these plants responded to environmental pollution stress. Sulphur isotopic composition in the transplanted *P. schreberi* was related to S concentrations in this species after 90 days of the experiment. Higher $\delta^{34}S$ values and S concentrations were noted in native mosses than in those transplanted from rural and urban sites while an opposite situation was reported in industrial sites. The transplanted *P. schreberi* was a better sulphur bioindicator than the native moss in more polluted industrial sites and worse in less polluted rural and urban sites.

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1. Introduction

Bioindication is a very useful way to assess the existence of environmental pollutants by measuring the levels of contaminants in plants (Markert et al., 2011). Mosses may be classified as the most effective organisms with ability to intercept, hold and accumulate xenobiotics (Fernándèz et al., 2000a, Fernándèz and Carballeira, 2001). Due to lack of cuticle and the presence of efficient cation exchange sites on their cell walls, shortage of a real root system or water-conducting tissues, they take most of the elements from airborne fallout being therefore a suitable tool for controlling atmospheric pollution (Galsomies et al., 1999; Fernándèz et al., 2000b; Gerdol et al., 2000, Carballeira and Fernándèz, 2002; Zechmeister et al., 2003). Mosses may be used in passive biomonitoring, i.e., using native species, and in active biomonitoring, using transplants in case of the absence of native mosses in the study areas (Fernándèz and Carballeira, 2001; Markert et al., 2003). However, plants have a capacity to adapt to certain environmental conditions. Therefore, it should be expected that native mosses accumulate less metals than the same species transplanted to polluted sites (Fernándèz and Carballeira, 2000a; Boquete et al. 2014). Thus native mosses may lead to underestimation of pollutant deposition. Complementary biomonitoring with native and transplanted mosses testing their response to sulphur deposition has not been studied so far. Therefore an experiment was set up based on the simplified and modified bioindication method of Fernándèz and Carballeira (2001) to compare the bioconcentration of sulphur and its stable isotope between the native moss *Pleurozium schreberi* from an industrial area with the bioconcentration in the same species transplanted from uncontaminated sites and equally exposed. Sulphur is one of the elements found in surplus in anthropogenically impacted areas, whose main sources are combustion of fossil fuels, processing of sulphur-containing ores, industry and less so vehicle exhaust

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emissions. Both anthropogenic and natural sources of atmospheric sulphur are distinguished by their stable isotopic signatures and expressed as δ values in units of per mille (‰) with respect to the Cañon Diablo Troilite (CDT or VCDT) international meteorite standard according to the following equation where $R = {}^{34}S/{}^{32}S$:

$$\delta^{34}S = \left[\frac{(R_{sample})}{R_{standard}} - 1\right] \times 100$$

(Wiseman and Wadleigh, 2002; Wadleigh, 2003). Approximately 95% of S in the environment occurs as the stable ^{32}S isotope, while 4.2% occurs as the heavier stable ^{34}S isotope. If an artificial source of S, such as air pollution, differs from the natural background levels in the relative amounts of these two isotopes, it provides a distinctive signature of this source when combined with the measured concentration of sulphur (de Caritat et al., 1997; Wadleigh, 2003; Sanborn et al., 2005; Derda et al., 2006). Therefore, the analysis of stable S isotope supply is a powerful tool for studying various aspects of the biogeochemical cycling of this element (de Caritat et al., 1997). Wadleigh (2003) studies illustrate the potential of combining stable isotopes with concentration measurements for lichen biomonitoring of atmospheric sulphur. Since mosses receive the bulk of their nutrients directly from wet and dry deposition, their sulphur isotopic composition should reflect that of the atmosphere (Krouse and Case, 1981). The present study compares the concentrations of total sulphur and the $\delta^{34}S$ isotope values of *P. schreberi* transplanted from a control site to rural, urban and industrial sites and the same species growing naturally at the same sites. According to Ares et al. (2012) the technique where live moss samples are exposed is frequently used to estimate the level of adaptation of native moss to contamination in a selected area. This helps with questions which arise when utilising native moss in which genotypic and/or phenotypic adaptation may develop in polluted environments with modified tissue concentrations of xenobiotics. We tested the hypothesis that the concentration of S in *P. schreberi* transplanted from an unpolluted control site to an industrial area reflects the level of deposited sulphur more closely than the same parameter in the native *P. schreberi*.

2. Materials and methods

2.1. Description of the investigated area

Investigations were carried out in one of the most polluted urban regions of Poland, in Upper Silesia (Fig. 1) characterised by

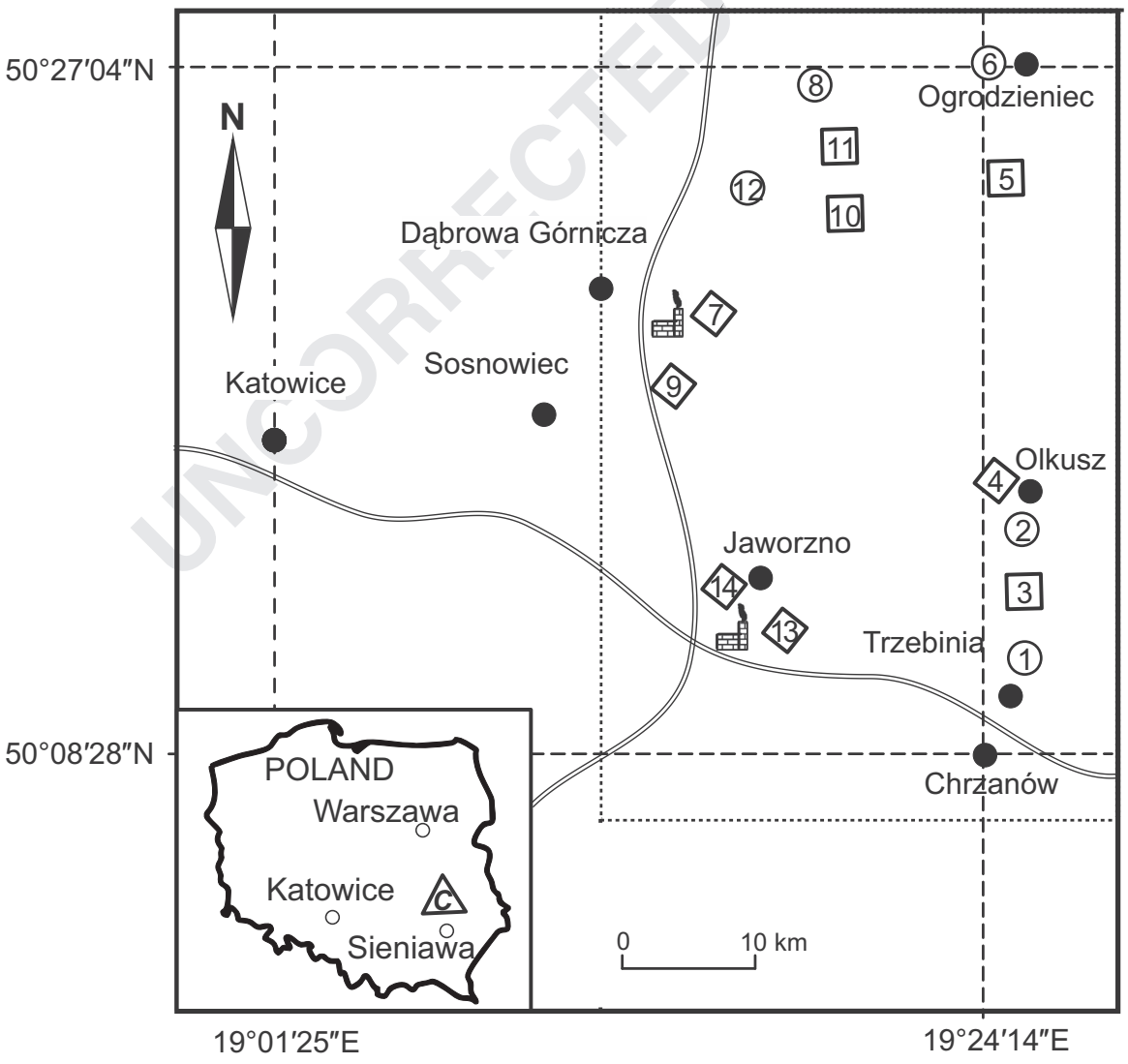

Fig. 1. Location of the investigated area. Symbols refer to: circle = urban, square = rural, diamond = industrial, triangle = control, ═══ highways or national roads; ---------- study area border; smelter or power station.

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hard coal mines and smelters (Pluta, 2001). This area receives emissions from local industry and heavy traffic but also from airborne transboundary pollution from Germany and the Czech Republic (Appleton et al., 2000). The primary aim of the present investigation was to test whether these massive sulphur emissions from those areas have left a recognisable, and thus traceable, sulphur isotopic signal in the environment, a task which, to our knowledge, has not been accomplished in this region before.

2.2. Collection of samples

Terrestrial, pleurocarpous and ectohydric *P. schreberi* (Brid.) Mitt. was selected because of its widespread occurrence in the Northern Hemisphere, including Poland. This species has proved to be a suitable bioindicator of metals (Samecka-Cymerman et al., 2006).

Samples of native and transplanted *P. schreberi* were collected within a rectangular area with a size of 27×48 km^2. The coordinates of the four corners of this rectangle are: northwest corner: 50°28′23″N; 19°11′14″E; northeast corner: 50°28′23″N; 19°34′16″E; southwest corner: 50°02′11″N; 19°11′14″E; southeast corner: 50°02′11″N; 19°34′16″E. The area was divided into 48 5×5 km^2 squares as recommended by Amblard-Gross et al. (2004). Of these 48 squares 14 were selected at random of which five from urban areas (no 1, 2, 6, 8 and 12), four from rural areas (no 3, 5, 10 and 11) and five from industrial areas (no 4, 7, 9, 13 and 14). Within the central part (5×5 km^2) of each of the 14 selected squares, three 2×2 m^2 subsquares, covered with *P. schreberi*, were selected at random for the collection of native moss samples (green parts of *P. schreberi* were taken only). Each plant sample consisted of a mixture of 3 subsamples. In each of the three 2×2 m^2 subsquares, three randomly chosen sites were cleared of vegetation, after which patches (20×20 cm^2) of *P. schreberi* (originating from an unpolluted control site) with a few millimetres of soil layer were transplanted (giving a total of $14 \times 3 = 42$ transplant replicates. The remaining part of the 2×2 m^2 subsquare was left covered by native *P. schreberi*. The moss carpet was recognised as protection which did not allow pollutants to infiltrate/pass through into and accumulate in soils (Case and Krouse, 1980). The unpolluted control site had 42 *P. schreberi* transplants, originating from a clearcut of a forest with *Pinus sylvestris* as the predominant tree, between Sieniawa and Adamówka, 200 km east of Katowice and 112 km south of Lublin (50°13′03″N; 22°43′53″E, Fig. 1). The experimental sites were selected in rural, urban and industrially influenced areas. No physiological damage was observed in the transplanted mosses in this study, either macroscopic or microscopic, over the duration of the experiment. The transplanted mosses were visually indistinguishable from those growing naturally in the control site (Wiseman and Wadleigh, 2002). The experiment lasted 90 days as in a preliminary investigation this exposure appeared to be long enough to allow comparison of bioconcentration in transplanted and native *P. schreberi*. The number of replicates was sufficient for proper statistical data interpretation. As required by Markert et al. (1996) and ICP Vegetation (2005), the collected mosses had not been exposed directly to canopy throughfall. Dead material, soil particles and litter were manually removed from the moss samples.

2.3. Analyses

The collected moss samples were frozen as soon as possible (−20 °C) to prevent bacterial activity. In the laboratory 10 g of wet moss mass was separated. The moss was washed briefly twice with redistilled water (Gałuszka, 2005; Skrzypek et al., 2008) to remove loosely attached dust and soluble sulphur forms deposited on the plant surface. Subsequently, the moss samples were vacuum-dried (freeze-dried in a Labogene ApS CoolSafe 55-4 lyophilizer, Denmark) and weighed. Finally, dry moss samples were homogenised in a mill and sealed in air-tight LDPE containers. Organic sulphur in the mosses was pre-concentrated using high pressure (2.5 MPa of oxygen) explosively combusted mineralisation in a Parr Bomb device (Parr Instrument Company, Moline, Illinois, USA) according to Siegfriedt et al. (1951). The solution was filtered and organic sulphur was recovered by precipitation from the hot solution as $BaSO_4$ at pH of about 2 (acidified with 18% HCl) by the addition of excess $BaCl_2$.

2.3.1. Isotopic analysis of organic sulphur in the moss

Stable sulphur isotope analyses were carried out using an off-line vacuum preparation technique. $BaSO_4$ was quantitatively converted to gaseous SO_2 in a reaction with V_2O_5 (Yanagisawa and Sakai, 1983) and then cryogenically purified off-line (Jędrysek et al., 2002). The $\delta^{34}S$ values of SO_2 representing organic sulphur were determined using a Delta Plus Advantage mass spectrometer. The resulting $\delta^{34}S$ values were presented relative to the international VCDT (Vienna Cañon Diablo Troilite) scale, where the $\delta^{34}S_{VCDT}$ value is defined as the relative difference, in parts per thousand (‰), between the isotope ratio of the sample and that of the standard. The isotope data were normalised using international IAEA standards (NBS-127, IAEA-SO-5 and IAEA-SO-6). The error of $\delta^{34}S$ determination (estimated from analyses of laboratory standards) was below 0.2‰.

Additionally all replicate samples were analysed for total S using SC 114-DR from LECO Corporation.

Stable sulphur isotope analyses were carried out in the Laboratory of Isotope Geology and Geoecology of the University of Wrocław.

2.4. Statistical analysis

Differences among the sampling sites in $\delta^{34}S$ values and sulphur concentrations in mosses were evaluated by one way ANOVA. The normality of the analysed features was checked using Shapiro–Wilk's *W* test, and the homogeneity of variances was checked using the Brown–Forsythe test (Brown and Forsythe, 1974, Argaç, 2004).

A post-hoc LSD test (Zar, 1999) was used to compare the $\delta^{34}S$ values and sulphur concentrations in the moss between the three groups of rural, urban and industrial sites (Sokal and Rohlf, 2003).

A *t*-test (Sokal and Rohlf, 2003; Zar, 1999) was used to compare $\delta^{34}S$ values and S concentrations in the native and transplanted moss after 0 and 90 days of exposure.

Pearson correlation coefficients were calculated (Sokal and Rohlf, 2003) to examine the relationships between the $\delta^{34}S$ values and sulphur concentrations in native and transplanted *P. schreberi*.

The calculations were done with Statistica 10 software (StatSoft, 2011).

3. Results and discussion

The ranges of $\delta^{34}S$ values and sulphur concentrations in the moss samples are shown in Table 1. The mean concentrations of $\delta^{34}S$ and sulphur in mosses from various sampling sites differed significantly (ANOVA $P < 0.05$).

In comparison to the concentrations of sulphur from a relatively pristine environment as observed by Poikolainen (2004) in mosses from Finland (960 mg kg^{-1}) and by Grodzińska and Godzik (1991) in mosses from Spitsbergen (561 mg kg^{-1}) S concentrations in all mosses in this investigation were higher (Table 1). Sulphur isotopic composition in mosses investigated by de Caritat et al. (1997) was from 6.0 to 8.4‰. These are data from the

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Table 1
Mean and Standard Deviation (SD) of S concentration (mg kg^{-1}) and δ^{34} S (‰) values in native and transplanted *P. schreberi* from 1 urban, 2 rural and 3 industrial sites after 0 and 90 days of exposure; $N=42$; Probability level (P) for t-test comparing S concentrations and δ^{34}S values in native and transplanted moss between 0 and 90 days of exposure.

	S native 0 day Mean ± SD	S native 90 days Mean ± SD	P	S transplant 0 day (control) Mean ± SD	S transplant 90 days Mean ± SD	P	δ^{34} S native 0 day Mean	δ^{34} S native 90 days Mean	P	δ^{34} S transplant 0 day (control) Mean	δ^{15} S transplant 90 days Mean	P
1	1868 ± 196	1862 ± 164	> 0.05	1534 ± 7.0	1603 ± 29	< 0.05	2.1 ± 0.2	2.3 ± 0.3	> 0.05	1.0 ± 0.01	1.6 ± 0.4	< 0.05
2	1898 ± 87	1919 ± 140	> 0.05	1528 ± 3.4	1649 ± 109	< 0.05	2.1 ± 0.2	2.1 ± 0.1	> 0.05	1.0 ± 0.01	1.5 ± 0.4	< 0.05
3	1986 ± 107	2113 ± 89	> 0.05	1551 ± 7.7	2360 ± 216	< 0.01	2.2 ± 0.3	2.6 ± 0.2	> 0.05	1.0 ± 0.01	3.6 ± 0.9	< 0.001

industrial Kola Peninsula region, with high emission loads of SO_2 and other xenobiotics in the atmosphere. In this investigation *P. schreberi* showed the highest δ^{34}S value at industrial site 7 (4.7‰) east from a steel smelter (in the direction of prevailing winds) and site 13 (4.3‰) affected by a complex of two power stations (Fig. 1). These highest δ^{34}S values corresponded to the δ^{34}S values presented by Gałuszka (2005) and Migaszewski et al. (2010) for *Hylocomium splendens* as 4.4–7.1‰, and for *P. schreberi* as 3.7–9.1‰ for an urban area. According to these authors such positive values point that mosses are considerably enriched with the ^{34}S isotope. This phenomenon in higher plants can be explained either by the uptake of SO_4^{-2} enriched in ^{34}S or by the production of H_2S depleted in ^{34}S in metabolic processes, finally enriched in ^{34}S residual organic sulphur (Case and Krouse, 1980; Rennenberg, 1991; Migaszewski and Pasławski, 1996; Gałuszka, 2005). Case and Krouse (1980) report excretion of isotopically lighter sulphur by lichens. However, the mechanisms involved in these processes in mosses are unknown, and the problem needs further investigation. Migaszewski et al. (2010) are of the opinion that δ^{34}S values (4.3–8.7‰) for *P. schreberi* from the Kola Peninsula and much higher (16–32‰) for the species from Alberta, Canada (Winner et al., 1978) suggest that there may be other sources of atmospheric sulphur and an influence of different ecological factors on sulphur accumulation northern Canada compared with those in Europe. A positive δ^{34}S signature of anthropogenic airborne sulphur accumulated by mosses is characteristic for central Europe (Migaszewski et al., 2010). Positive signatures of δ^{34}S for *P. schreberi* not only from industrial but also from all rural and urban sites may be caused by domestic coal based heating systems and transportation exhausts (Norman et al., 2004; Gałuszka, 2005; Migaszewski et al., 2010; Xiao et al., 2010a). The sulphur isotope was established as −1 to +8‰ (most data are from +3.5 to +7‰) in coal and from +2 to+15‰ in lignite of Polish origin (Chmielewski et al., 2002; Derda et al., 2006). Additionally δ^{34}S in rainfall deposition being a source of sulphur for mosses was from 2.5‰ to 3.0‰ (southwest Poland), 6‰ (south-central Poland), from 4 to 5‰ (southeast Germany) and from 7 to 8‰ (north Czech Republic) (Jędrysek, 2000; Tichomirowa et al., 2007; Górka et al., 2008; Migaszewski et al., 2010; Górka et al., 2011). The δ^{34}S values reported for gasoline and diesel in Canada varied from +5 to +9‰ for fuel sulphur and exhaust products of its combustion (Norman et al., 2004). In our area depletion in ^{34}S organic sulphur in *P. schreberi* compared to the average δ^{34}S values in coal or rain may be caused by desulphurisation units in smelters which change the isotopic ratio of sulphur in the outlet gas streams depleting the heavy 34 isotope (Derda et al., 2006, 2007). These authors established a δ^{34}S value of +1.6‰ before desulphurisation and -4.0‰ after desulphurisation for Bełchatów lignite exhaust gases. To add possible fractionation of sulphur in industrial processes if the a plant lacks a desulphurisation unit the final sulphur isotopic signal of SO_2/SO_4^{2-} will correspond to a sulphur signal in the fuel. However, a desulphurisation unit can shift the final sulphur isotopic signal and deplete the SO_2/SO_4^{2-} ratio to about 6% compared to the fuel used (Derda et al., 2006, 2007).

A post-hoc LSD test ($P<0.05$) revealed that in comparison with rural and urban sites the highest δ^{34}S values and S concentrations were found in industrial sites for both native and transplanted mosses after 90 days of exposure. There was no difference in δ^{34}S values and S concentrations between rural and urban sites. This is in agreement with Xiao et al. (2010b) and Liu et al. (2011) who observed no significant difference between urban and rural areas indicating that the atmosphere over both types of sites was polluted by S.

There was a significant Pearson correlation between δ^{34}S values and S concentrations in native ($P<0.05$) and transplanted mosses ($P<0.01$) after 90 days of exposure which was in agreement with de Caritat et al. (1997) that sulphur isotopic composition in many moss species was related to that of atmospheric S compounds. According to these authors this relation was probably caused by the direct uptake of sulphur compounds without preference for one of the isotopic forms (de Caritat et al., 1997). Skrzypek et al. (2010) believes that mosses do not have the ability to restrict sulphur uptake. In these plants, sulphur concentration and stable sulphur isotope composition are kept at equilibrium with the concentration and stable sulphur isotope composition in the environment. Mosses keep the source-specific sulphur isotopic signature similar to that of the atmosphere being their main source of sulphur (Xiao et al., 2010a). According to these authors the similar values of stable isotopes in fossil fuels and mosses suggests a considerable contribution of them being burnt locally to atmospheric S. This phenomenon may be used to explain regional δ^{34}S differences (Xiao et al., 2010a). According to Liu et al. (2011) the major source of anthropogenic S and their δ^{34}S values in the city environment was strongly associated with those in fossil fuels used by industries and residents. Mosses can be used for the evaluation of airborne sulphur because of their very close sulphur and δ^{34}S relation and tissue sulphur being coherent with atmospheric SO_2 (Liu et al., 2009).

The t-test revealed no significant difference in δ^{34}S values and S concentrations between native mosses at the beginning of the experiment and after 90 days of exposure. However, significantly higher δ^{34}S values and S concentrations in transplanted mosses were present after 90 days in comparison with the beginning of the experiment (Table 1).

Results of the bioaccumulation of sulphur by *P. schreberi* were partly different. The t test revealed that δ^{34}S values and S concentrations were higher in native mosses than in transplants from rural ($P<0.05$) and urban ($P<0.01$) sites (Fig. 2) and an opposite phenomenon was observed in industrial sites ($P<0.05$) with δ^{34}S values and S concentrations higher in transplants than in native mosses (Fig. 2). Our results for rural and urban sites are in contradiction with Fernándèz et al. (2000b) who were of the opinion that plants have an ability to adjust to environmental conditions. Their investigation on Hg accumulation by *Scleropodium purum* as

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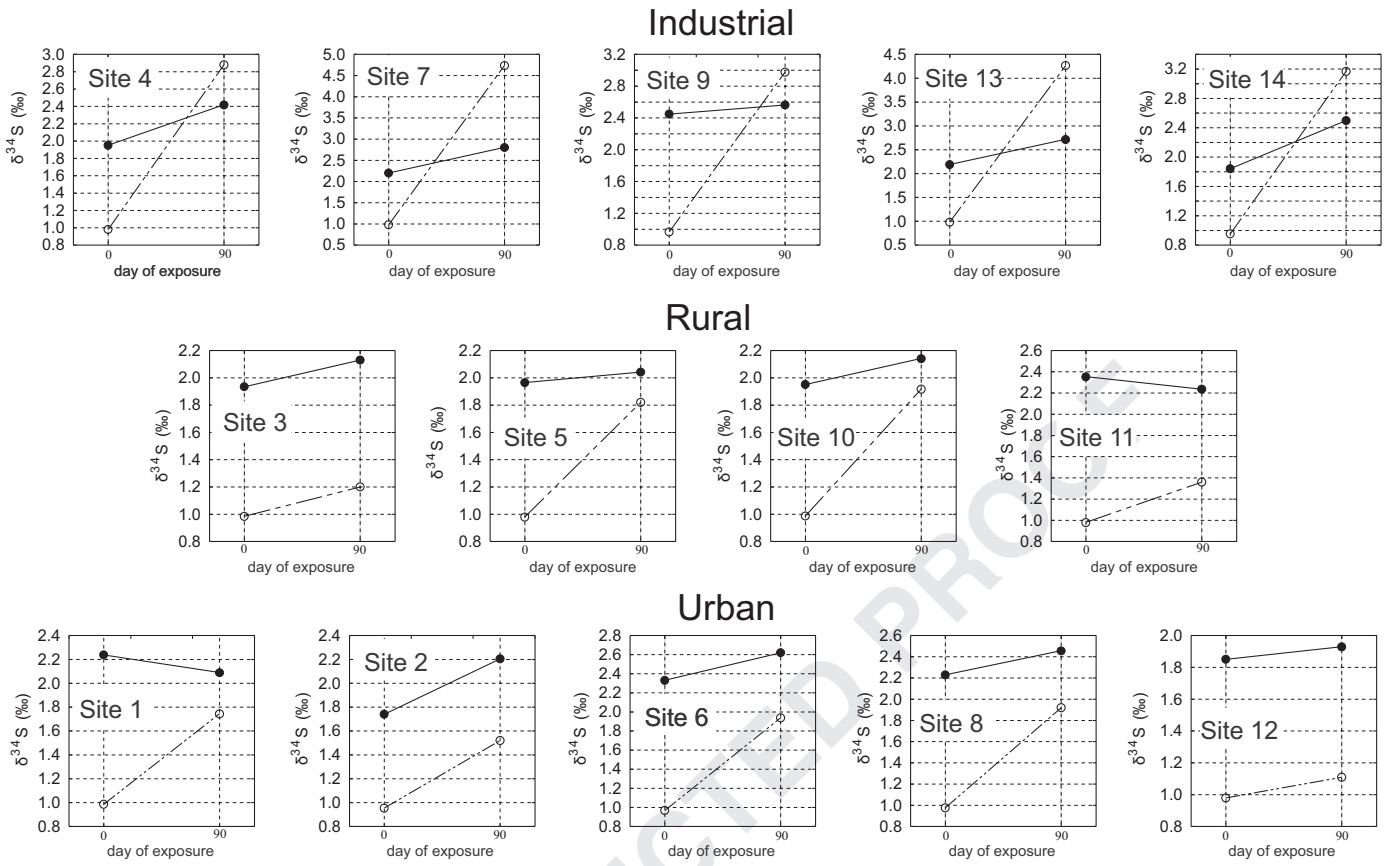

Fig. 2. $\delta^{34}S$ (‰) values in *Pleurozium schreberi* after 0 and 90 days of exposure in: native mosses —●— and transplanted mosses —⊖— from industrial, rural and urban sites. The concentration of metals on day 0 in the transplanted *Pleurozium schreberi* is represented by the value in the moss at the control site from which the transplanted mosses were collected.

well as a study of Samecka-Cymerman and Kempers (2007) on metal accumulation by *Pohlia nutans* suggest that native mosses accumulated significantly less metals than transplanted individuals of the same species. Also Boquete et al. (2014) report that native *Pseudoscleropodium purum* from polluted areas develop mechanisms of lower uptake or higher release of metals in comparison with the same species transplanted from clean sites, which helps these plants to reduce or overcome the effects of metal toxicity in their organism. The discrepancies may result from using different elements and different moss species by the respective authors. Rao (1982) reports that various species of terrestrial mosses block the uptake of the xenobiotics to which they are exposed, which allows them to survive in unfavourable conditions. According to Boquete et al. (2014) mosses growing in contaminated areas adapt to xenobiotics and are able to overcome their toxic effects. Better accumulation of sulphur compounds by *P. schreberi* from industrial in comparison with rural and urban sites may probably be explained by a phenomenon described by Case and Krouse (1980) for lichens by selective excretion of isotopically lighter sulphur when concentrations in tissue exceed a certain value. In this investigation industrial mosses contained 2094–2688 mg kg^{-1} S, much more than the 1400 mg kg^{-1} threshold of Case and Krouse (1980). However, further investigation is necessary to explain this problem. Results of this investigation indicate that isotopic signatures of S in *P. schreberi* may be used as a fingerprint (Xiao et al., 2011) to describe atmospheric sulphur sources.

4. Conclusions

Positive $\delta^{34}S$ values up to 4.7‰ in *P. schreberi* not only from industrial sites but also from rural and urban sites show that the mosses tested were considerably enriched in ^{34}S.

$\delta^{34}S$ values and S concentrations were higher in native than in transplanted mosses from rural and urban sites while those in transplanted mosses where higher than in native mosses from industrial sites.

The transplanted *P. schreberi* was a better sulphur bioindicator than the native moss in more polluted industrial sites and worse in less polluted rural and urban sites.

These results provide a reference for the future monitoring of sulphur pollution with *P. schreberi* and explain which method (native or transplants) should be applied taking into consideration the type (rural, urban or industrial) of the area of interest.

Uncited references

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Kłos et al. (2011); Kosior et al. (2010).

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References

Amblard-Gross, G., Maul, A., Ferard, J.F., Carrot, F., Ayrault, S., 2004. Spatial variability of sampling: grid size impact on atmospheric metals and trace elements deposition mapping with mosses. J. Atmos. Chem. 49, 39–52.

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Appleton, J., Lee, K.M., Sawicka-Kapusta, K., Damek, M., Cookec., M., 2000. The heavy metal content of the teeth of the bank vole (*Clethrionomys glareolus*) as an exposure marker of environmental pollution in Poland. Environ. Pollut. 110, 441–449.

Argaç, D., 2004. Testing for homogeneity in a general one-way classification with fixed effects: power simulations and comparative study. Comput. Stat. Data Anal. 44, 603–612.

Boquete, M.T., Bermúdez-Crespo, J., Aboal, J.R., Carballeira, A., Fernández, J.Á., 2014. Assessing the effects of heavy metal contamination on the proteome of the moss *Pseudoscleropodium purum* cross-transplanted between different areas. Environ. Sci. Pollut. Res. 21, 2191–2200.

Brown, M.B., Forsythe, A.B., 1974. Robust tests for the equality of variances. J. Am. Stat. Assoc. 69, 364–367.

Carballeira, A., Fernándèz, J.A., 2002. Bioconcentration of metals in the moss *Scleropodium purum* in the area surrounding a power plant. A geotopographical predictive model for mercury. Chemosphere 47, 1041–1048.

Case, J.W., Krouse, H.R., 1980. Variations in sulphur content and stable sulphur isotope composition of vegetation near a SO_2 source at Fox Creek, Alberta, Canada. Oecologia 44, 248–257.

Chmielewski, A.G., Wierzchnicki, R., Derda, M., Mikołajczuk, A., 2002. Sulfur isotope composition of selected Polish coals. Nukleonika 47, 67–68.

de Caritat, P., Krouse, H.R., Hutcheon, I., 1997. Sulphur isotope composition of stremwater, moss and humus from eight arctic catchments in the Kola peninsula Region (NW Russia, N Finland, NE Norway). Water Air Soil Pollut. 94, 191–208.

Derda, M., Chmielewski, M.G., Licki, J., 2006. Stable isotopes of sulphur in investigating pollution sources. Environ. Prot. Eng. 32 (3), 63–68.

Derda, M., Chmielewski, A.G., Licki, J., 2007. Sulphur isotope compositions of components of coal and S-isotope fractionation during its combustion and flue gas desulphurization. Isot. Environ. Health Stud. 43, 57–63.

Fernándèz, J.A., Carballeira, A., 2001. A comparison of indigenous mosses and topsoils for use in monitoring atmospheric heavy metal deposition in Galicia (northwest Spain). Environ. Pollut. 114, 431–441.

Fernándèz, J.A., Aboal, J.R., Carballeira, A., 2000a. Use native and transplanted mosses as complementary techniques for biomonitoring mercury around an industrial facility. Sci. Total Environ. 256, 151–161.

Fernándèz, J.A., Rey, A., Carballeira, A., 2000b. Differences in the responses of native and transplanted mosses to atmospheric pollution: a possible role of selenium. Environ. Pollut. 110, 73–78.

Galsomies, L., Letrouit, M.A., Deschamps, C., Savanne, D., Avnaim, M., 1999. Atmospheric metal deposition in France: initial results on moss calibration from the 1996 biomonitoring. Sci. Total Environ. 232, 39–47.

Gałuszka, A., 2005. The chemistry of soils, rocks and plant bioindicators in three ecosystems of the Holy Cross mountains, Poland. Environ. Monit. Assess. 110, 55–70.

Gerdol, R., Bragazza, L., Marchesini, R., Alber, R., Bonetti, L., Lorenzoni, G., Achilli, M., Buffoni, A., De Marco, N., Franchi, M., Pison, S., Giaquinta, S., Palmieri, F., Spezzanto, P., 2000. Monitoring of heavy metal deposition in Northern Italy by moss analysis. Environ. Pollut. 108, 201–208.

Górka, M., Jędrysek, M.O., Strąpoć, D., 2008. Isotopic composition of sulphates from meteoric precipitation as an indicator of pollutant origin in Wrocław (SW Poland). Isot. Environ.Health Stud. 44, 177–188.

Q4 Górka, M., Hałas, S., Strąpoć, D., Kufka, D., Jędrysek, M.O., 2011. 5-years (2004–2009) isotopic seasonal observations of the sulphates in Wrocław (SW Poland) precipitation. In: Proceedings of the conference of European Society for Isotope Research, Central European Geology, Acta Geol. Hun. 54, 39.

Grodzińska, K., Godzik, B., 1991. Heavy metals and sulphur in mosses from Southern Spitsbergen. Polar Res. 9, 133–140.

ICP Vegetation: Heavy metals in European mosses: 2005/2006 survey, 2005. Monitoring Manual. UNECE ICP Vegetation Coordination Centre, CEH Bangor, UK.

Jędrysek, M.O., 2000. Oxygen and sulphur isotope dynamics in the SO_4^{2-} of an urban precipitation. Water Air Soil Pollut. 117, 15–25.

Jędrysek, M.O., Kaluzny, A., Hoefs, J., 2002. Sulphur and oxygen isotope ratios in spruce needles as a tracer of atmospheric pollution. J. Geophys. Res. 107 (D18), 4353.

Kłos, A., Rajfur, M., Wacławek, M., 2011. Application of enrichment factor (EF) to the interpretation of results from the biomonitoring studies. Ecol. Chem. Eng. S 18, 171–183.

Kosior, G., Samecka-Cymerman, A., Kolon, K., Kempers, A.J., 2010. Bioindication capacity of metal pollution of native and transplanted *Pleurozium schreberi* under various levels of pollution. Chemosphere 81, 321–326.

Krouse, H.R., Case, J.W., 1981. Sulphur isotope ratios in water, air, soil and vegetation near Teepee Creek gas plant, Alberta. Water Air Soil Pollut. 15, 11–28.

Liu, X.Y., Xiao, H.Y., Liu, C.Q., Xiao, H.W., Wang, Y.L., 2009. Assessment of atmospheric sulfur with the epilithic moss *Haplocladium microphyllum*: evidences from tissue sulfur and $\delta^{34}S$ analysis. Environ. Pollut. 157, 2066–2071.

Liu, X.Y., Xiao, H.Y., Liu, C.Q., 2011. Physiological and isotopic signals in epilithic mosses for indicating anthropogenic sulfur on the urban-rural scale. Ecol. Indic. 11, 1245–1250.

Markert, B., Herpin, U., Siewers, U., Berlekamp, J., Lieth, H., 1996. The German heavy metal survey by means of mosses. Sci. Total Environ. 182, 159–168.

Markert, B.A., Wuenschmann, S., Fraenzle, S., Figueiredo, A.M.G., Ribeiro, A.P., Wang, M., 2011. Bioindication of atmospheric trace metals-with special references to megacities. Environ. Pollut. 159, 1991–1995.

Migaszewski, Z.M., Dołęgowska, S., Hałas, S., Trembaczowski, A., 2010. Stable sulphur isotope ratios in the moss species *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from the Kielce area (south-central Poland). Isot. Environ. Health Stud. 46, 219–224.

Norman, A.L., Belzer, W., Barrie, L.A., 2004. Insights into the biogenic contribution to aerosol total sulphate and precipitation in the Fraser Valley afforded by isotopes of sulphur and oxygen. J. Geophys. Res. D5 (109), D05311.

Pluta, I., 2001. Barium and radium discharged from coal mines in the Upper Silesia, Poland. Environ. Geol. 40 (3), 345–348.

Poikolainen, J., 2004. Mosses, epiphytic lichens and tree bark as biomonitors for air pollutants-specifically for heavy metals in regional surveys. University of Oulu, Oulun Yliopisto, Oulu, Ph.D. thesis.

Rao, D.N., 1982. Responses of bryophytes to air pollution. In: Smith, A.J.E. (Ed.), Bryophyte Ecology, 7. Chapman and Hall, London, pp. 445–471.

Samecka-Cymerman, A., Kosior, G., Kempers, A.J., 2006. Comparison of the moss *Pleurozium schreberi* with needles and bark of *Pinus sylvestris* as biomonitors of pollution by industry in Stalowa Wola (southeast Poland). Ecotoxicol. Environ. Saf. 65, 108–117.

Samecka-Cymerman, A., Kempers, A.J., 2007. Differences in concentration of heavy metals between native and transplanted *Pohlia nutans* (Hedw.) Lindb.-a case study from a dump exposed to industrial emissions in Poland. Pol. J. Environ. Stud. 16, 251–258.

Sanborn, P., Brockley, R., Mayer, B., Yun, M., Prietzel, J., 2005. Sulphur fertilization of Q5 lodgepole pine: a stable isotope tracer study (E.P. 886.15): establishment report. British Columbia Ministry of Forests, Res. Br. Victoria, B.C., p. 52.

Siegfriedt, R., Wiberley, S., Moore, R., 1951. Determination of sulphur after combustion in a small oxygen bomb. Anal. Chem. 23, 1008–1011.

Skrzypek, G., Akagi, T., Drzewiecki, W., Jędrysek, M.O., 2008. Stable isotope studies of moss sulfur and sulfate from bog surface waters. Geochem. J. 42, 481–492.

Skrzypek, G., Jezierski, P., Szynkiewicz, A., 2010. Preservation of primary stable isotope signatures of peat-forming plants during early decomposition-observation along an altitudinal transect. Chem. Geol. 273, 238–249.

Sokal, R.R., Rohlf, F.J., 2003. Biometry: The Principles and Practice of Statistics in Biological Research. Freeman and Company, New York.

StatSoft, Inc. 2011. STATISTICA (data analysis software system), version 10, ⟨www.statsoft.com⟩.

Tichomirowa, M., Haubrich, F., Klein, M., Matschullat, J., 2007. Regional and temporal (1992–2004) evolution of air-borne sulphur isotope composition in Saxony, southeastern Germany central Europe. Isot. Environ. Health Stud. 43, 295–305.

Wadleigh, M.A., 2003. Lichens and atmospheric sulphur: what stable isotopes reveal. Environ. Pollut 126, 345–351.

Winner, W.E., Bewley, J.D., Krouse, H.R., 1978. Stable sulfur isotope analysis of SO_2 pollution impact on vegetation. Oecologia 36, 351.

Wiseman, R.D., Wadleigh, M.A., 2002. Lichen response to changes in atmospheric sulphur: isotopic evidence. Environ. Pollut. 116, 235–241.

Xiao, H.Y., Tang, C.G., Xiao, H.W., Wang, Y.L., Liu, X.Y., Liu, C.Q., 2010a. Tissue S/N ratios and stable isotopes ($\delta^{34}S$ and $\delta^{15}N$) of epilithic mosses (*Haplocladium microphyllum*) for showing air pollution in urban cities in Southern China. Environ. Pollut. 158, 1726–1732.

Xiao, H.Y., Tang, C.G., Xiao, H.W., Liu, X.Y., Liu, C.Q., 2010b. Stable sulphur and nitrogen isotopes of the moss *Haplocladium microphyllum* at urban, rural and forested sites. Atmos. Environ. 44, 4312–4317.

Xiao, H.Y., Tang, C.G., Zhu, R.G., Wang, Y.L., Xiao, H.W., Liu, C.Q., 2011. Tracing sources of coal combustion using stable sulfur isotope ratios in epilithic mosses and coals from China. J. Environ. Monit. 13, 2243–2249.

Yanagisawa, F., Sakai, H., 1983. Preparation of SO_2 for sulfur isotope ratio measurements by thermal decompositions of $BaSO_4$–V_2O_5–SiO_2 mixtures. Anal. Chem. 55, 985–987.

Zar, H., 1999. Biostatistical Analysis. Prentice Hall, Upper Saddle River, New Jersey.

Zechmeister, H.G., Hohenwallner, D., Riss, A., Hanus-Illnar, A., 2003. Variations in heavy metal concentrations in the moss species *Abietinella abietina* (Hedw.) Fleisch. according to sampling time, within site variability and increase in biomass. Sci. Total Environ. 301, 55–65.

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