

HIGH SULFUR CONTAMINATION EFFECT ON THE ENVIRONMENT AT THE AFFORESTED FORMER JEZIÓRKO SULFUR MINE¹

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Abstract: Sulfur contamination of topsoil (0-20 cm), spatial distribution of contamination, surface water chemistry, growth reaction, vitality, and mineral supply of Common birch (*Betula pendula* Roth.) and Scots pine (*Pinus sylvestris* L.) as well as chemical composition of this and wood small-reed (*Calamagrostis epigejos* L.) were investigated on an area of over 200 ha of an afforested ecosystem after borehole sulfur mining. The chemistry dynamics of soil leaching and the remediation effect of the birch and pine litter were assayed in an experiment under controlled conditions. It was found that hot-spots with high sulfur concentration in soil reaching even 45,000 mg kg⁻¹, pH below 2.0 were still reported, however, it occupied hardly 2% of the researched area. Surface waters were characterized by an excessive concentration of sulfate ions (average 935.13 mg·L⁻¹) and calcium ions (up to 434 mg·L⁻¹), which was connected with the sulfur mining process and sludge lime used in neutralization. Wood small-reed was found to adapt well to the conditions of elevated sulfur concentration. The experiment confirmed that the addition of organic matter had a significant impact on the chemistry of soil solutions but did not indicate a remediation effect by increased sulfur leaching. The aim of the paper was a comprehensive study of the soil, surface water, and reaction of the plant to high sulfur concentration in soil on former Jeziórko sulfur mine. Soil contamination, plant chemistry, and their reaction were analyzed on 200 ha area (spatially) and at detailed study plots, represented various categories of plant cover. The chemistry of water was an additional element analyzed on independent sampling points (15) localized on streams and ponds on 200 ha reclaimed area.

Additional Key Words: sulfur, reclamation, plant chemistry, soil contamination

¹ Oral paper presented at the 2019 National Meeting of the American Society of Mining and Reclamation, Big Sky, MT. Welcome Back to Montana: The Land of Reclamation Pioneers, June 3–7, 2019. Published by ASMR, 1305 Weathervane Dr., Champaign, IL 61821.

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DOI: <http://dx.doi.org/10.21000/JASMR19030066>

Introduction

Around the world, sulfur was exploited in mines in the USA until 2000, and Iraq until 2003, according to TSI, 2019. Currently, Poland is the only country where native sulfur is extracted on a large scale (Osiek Mine since 1993) and international sources indicated that sulfur is exploited in Mexico since 2010; (TSI, 2019). Sulfur deposits occur in southern Poland, in the areas near Tarnobrzeg, Staszów, and Lubaczów PGI, (Polish Geological Institute, 2019). Sulfur extraction takes place in two methods: open strip-mining method and borehole method (Frasch method). In Poland, sulfur deposits were first extracted in the 1960s using the open strip-mining method (Piaseczno Mine and Machów Mine), and next the borehole Frasch method (Likus-Cieślik et al., 2015, 2017). This method of melting an underground sulfur deposit was patented by Herman Frasch in 1894 in the United States. It involves an injection of superheated water at a temperature of 140–160 °C into a sulfur field. Areas after sulfur extraction using the Frasch method are strongly transformed due to flooding and subsidence. Acidification of soil and groundwater, as well as the risk of Acid Mine Drainage (AMD), were the most important transformations from the underground sulfur extraction method. A particularly important transformation was strong soil sulfidation (reaching even 4%, Likus-Cieślik et al., 2017) caused by liquid sulfur leaked out. These types of areas are difficult to reclaim. Forest tree species are introduced in the reclamation treatment process into conditions that are different from natural habitats. High sulfur concentration results in an increase of nutrient leaching into the soil profile, the displacement of base cations Ca^{2+} and Mg^{2+} from the sorption complex which eventually leads to soil acidity. This process increases the mobility of trace elements that are harmful firstly to soil organisms and which subsequently disturb biogeochemical cycles and vascular plant nutrition (Menz and Seip, 2004). The excessive impact of SO_2 on vascular plants is demonstrated by negative effects on the root system, foliage, and in tissue damage (Rinne et al., 2010; Marcshner, 2012; Wei et al., 2017). As a result of dust from industrial emissions that settles on leaves, plant stomata are clogged, and hence, the processes of photosynthesis and transpiration are disturbed (Feliciano et al., 2001; Wei et al., 2017). In the case of trees, this leads to a reduction of leaf number, thinning of tree crowns, deformed canopy shape, and limited growth (Tomlinson, 1983). Sulfurous and acidic soils with close geochemical transformations occur also in industrialized regions, especially in the USA, Canada, Southern China, and in places located in the vicinity of sulfur mines or sour gas processing plants and former lignite coal mining sites (Katzur and Haubold-Rosar, 1996; Larssen and Carmichael,

2000; Liu et al., 2010). In areas affected by lignite mining, with Miocene deposits (associated with pyrites and marcasites) and in areas with iron and gold mines, high sulfur contamination is often associated with Fe, Al, or $\text{Fe}_2(\text{SO}_4)_3$ (Katzur and Haubold-Rosar, 1996; Katzur and Liebner, 1998; Grande et al., 2010). In agricultural soils, sulfur concentration should not exceed 500 mg kg^{-1} (EMA 1996). However, in agricultural areas, sulfur deficiencies are recorded (Zhao et al., 2002; Li et al., 2017). The correct supply of sulfur to the plant is necessary for their proper growth (Marschner, 2012).

The concentration of sulfur oxides in the air decreased by 74% between 1990 and 2011 especially after the EU's efforts to minimize negative emission of SO_2 (EEA, 2017). Decreases of SO_x (SO_2 and SO_3) is owed to fuel-switching in energy-related sectors away from high-sulfur solid and liquid fuels to low-sulfur fuels such as natural gas, the fitting of flue gas desulfurization abatement technology in industrial facilities, and the impact of European Union directives relating to the sulfur concentration of certain liquid fuels (EEA, 2017).

The aim of the work was a comprehensive study of the soils, surface waters, and reactions of trees and herbaceous plants in the restored forest ecosystem on the former sulfur mine. The former sulfur mine afforested taka place around 216 ha. The purpose of this comprehensive study of the ecosystem sampled was carried out in steps in a scheme from general to particular. Firstly, i) spatial distribution of sulfur, pH, and plant cover was determined on the whole researched area; ii) the surface water chemistry was assayed; iii) foliage chemistry and macronutrient supply of herbaceous plant and trees were analyzed; iv) and experiment under controlled condition regarding chemistry of soil solution in the leaching was carried out. The data are based on collected preliminary study results that were partly and separately published.

Materials and methods

Study site

The study was conducted on reclaimed and afforested post-mining areas of the former Jeziórko sulfur mine (FJSM), located in Southern Poland, near Tarnobrzeg ($50^{\circ}32'34 \text{ N}$, $21^{\circ}47'46 \text{ E}$) (Fig. 1). The region has an average annual temperature of $+8.2 \text{ }^{\circ}\text{C}$ ($-1.6 \text{ }^{\circ}\text{C}$ in January, and $+18.7 \text{ }^{\circ}\text{C}$ in July) and average annual precipitation ranges from 550 to 650 mm. The growing season lasts from 200 to 220 days per annum.

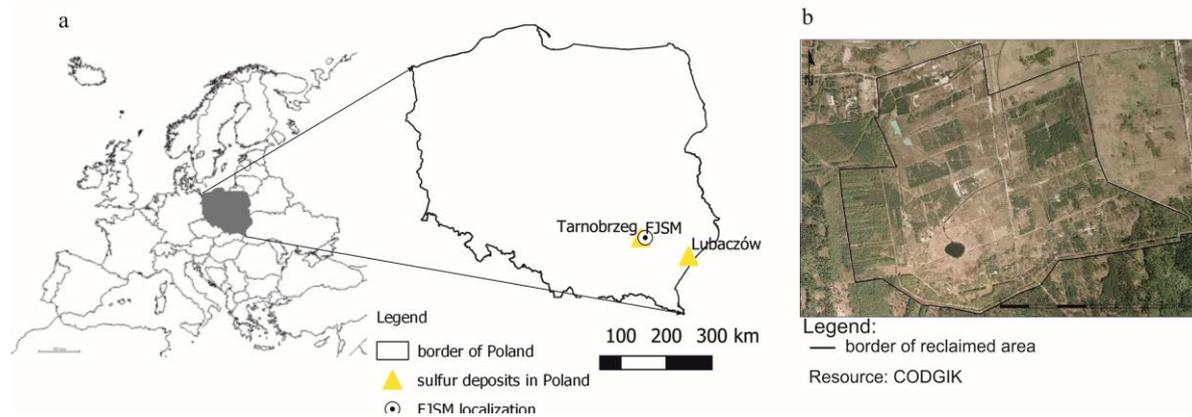


Figure 1. General overview to research area location (a, b) and reclaimed and afforested area border.

During the FJSM reclamation (1993 to 2010) removing the mine infrastructure (such as mine wells, pipelines, and access roads), improvements to hydrographic conditions and landscaping, pH neutralization of sulfurous, and excessively acidic soils by liming (average 400-500 Mg ha⁻¹), fertilization (70 kg ha⁻¹ P₂O₅, 60 kg ha⁻¹ K₂O) has been completed, and grass seed has been sown (Likus-Cieślak et al., 2017). Of over 2,000 ha previously occupied by the mine, over 700 hectares in total were reforested, of which 216.5 hectares, where this research was conducted, are currently managed by Nowa Dęba Forest Inspectorate, State Forest National Forest Holding (Fig. 1b). These treatments were followed by reforestation, mainly with one-year-old Scots pine seedlings (*Pinus sylvestris* L.) and an admixture of silver birch (*Betula pendula* Roth), and boreal oak (*Quercus rubra* L.; Likus-Cieślak et al., 2015). The general overview of the main species (Scots pine and silver birch 22 years old) in the current age shows in Fig. 2 and 3.

Field and laboratory work

The assessment of sulfur distribution and contamination. In order to comprehensively investigate the reclaimed and afforested area (about 216 ha) partial tasks were carried out. Firstly, a total of 88 sampling points were located in the FJSM in a regular grid of squares with sides measuring 150 m (Fig. 4). The points were first identified on the map using ArcGIS software (ESRI, Redlands, CA, USA), and then targeted and located using a Garmin GPS receiver (GPSMAP® 60CSx, Garmin Ltd., Olathe, KS, USA).



Figure 2. Overview to Scots pine stands in 2017 (22 years old of a stand).



Figure 3. Overview to Common birch stands in 2017 (22 years old of a stand).

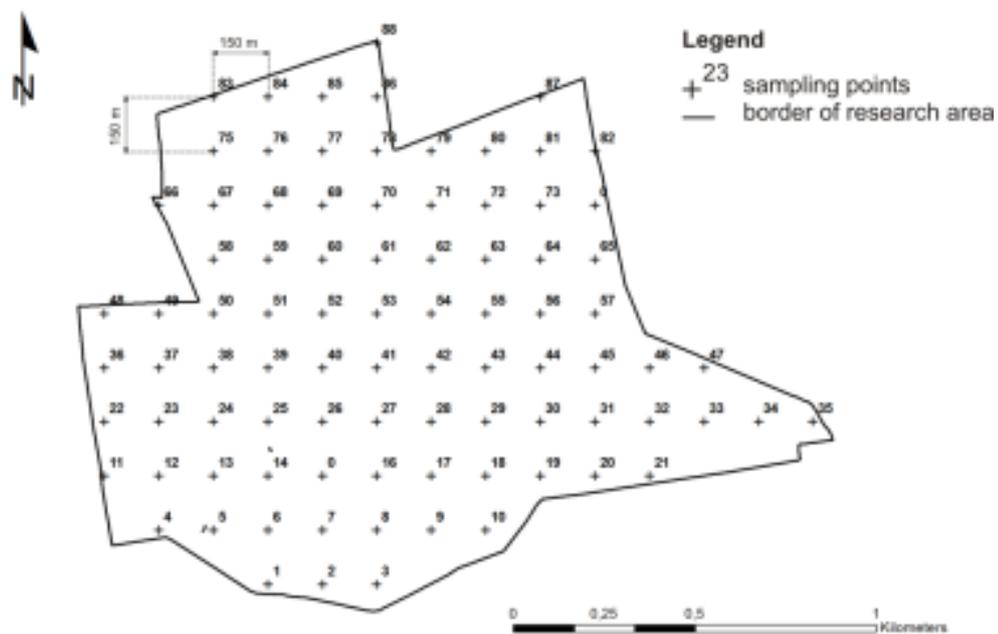


Figure 4. Distribution of sampling points on reclaimed and afforested the FSMJ site (Likus-Cieślík et al., 2017).

At the points, soil samples were collected from the top layer (0-20 cm). The pH was measured potentiometrically in 1 mol·L⁻¹ KCl (maintaining a ratio of soil: solution 1: 2.5), EC (soil ratio: solution 1: 5), and S_T with the TruMac Leco CNS analyzer (Leco Corporation, Saint Joseph, MI, USA) were measured. Currently, the guidelines respecting excessive sulfur concentration in Poland and Europe do not exist because reverse tendency – S in agricultural soil is in deficit. In this case, the degree of soil sulfur contamination was assessed on the basis of the guidelines of the Institute of Soil Cultivation and Fertilization Institute of Crop and Soil Fertilization (Kabata-Pendias et al., 1995). Spatial imaging (map compositions, Fig. 2, 5) of variations in the studied soil features, i.e., sulfur concentration in the soil, pH, and EC and herbaceous and woody vegetation surface coverage was done using the IDW (Inverse Distance Weighted) interpolation algorithm in ArcMap ArcGIS 10.2 (ESRI, Redlands, CA, USA).

Surface water chemistry

Samples of surface water were collected from 15 monitoring points on reservoirs and watercourses (Fig. 5, 6) four times a year. The waters were subjected to chemical analyses in which the pH, EC, and ionic composition (Ca²⁺, SO₄²⁻) were determined using a Dionex Ion Chromatography 5000 apparatus (Thermo Fisher Scientific, Waltham, MA, USA).

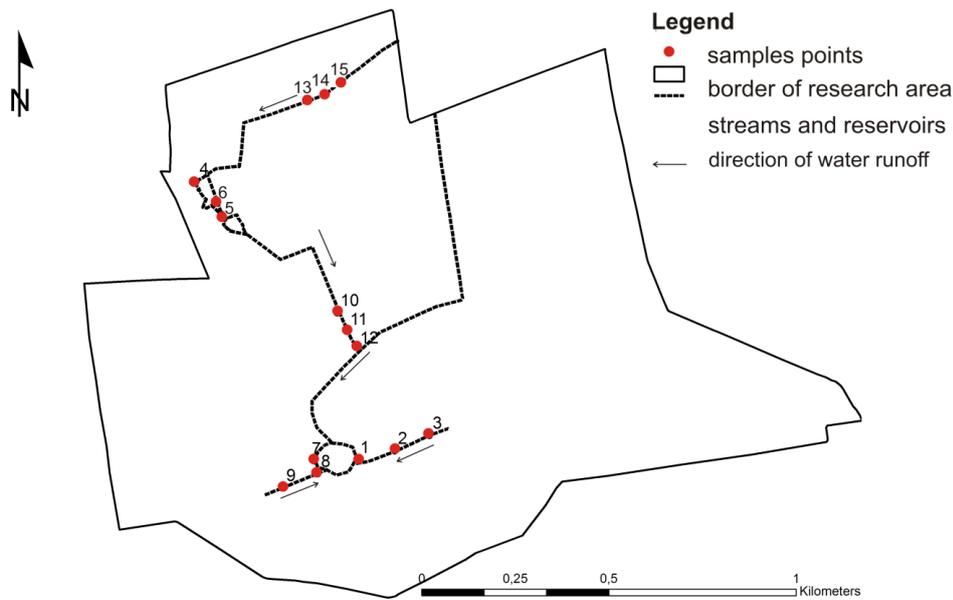


Figure 5. Distribution of surface water sampling points from the watercourse reservoir in reclaimed and afforested FSMJ site (Likus-Cieřlik et al., 2019).



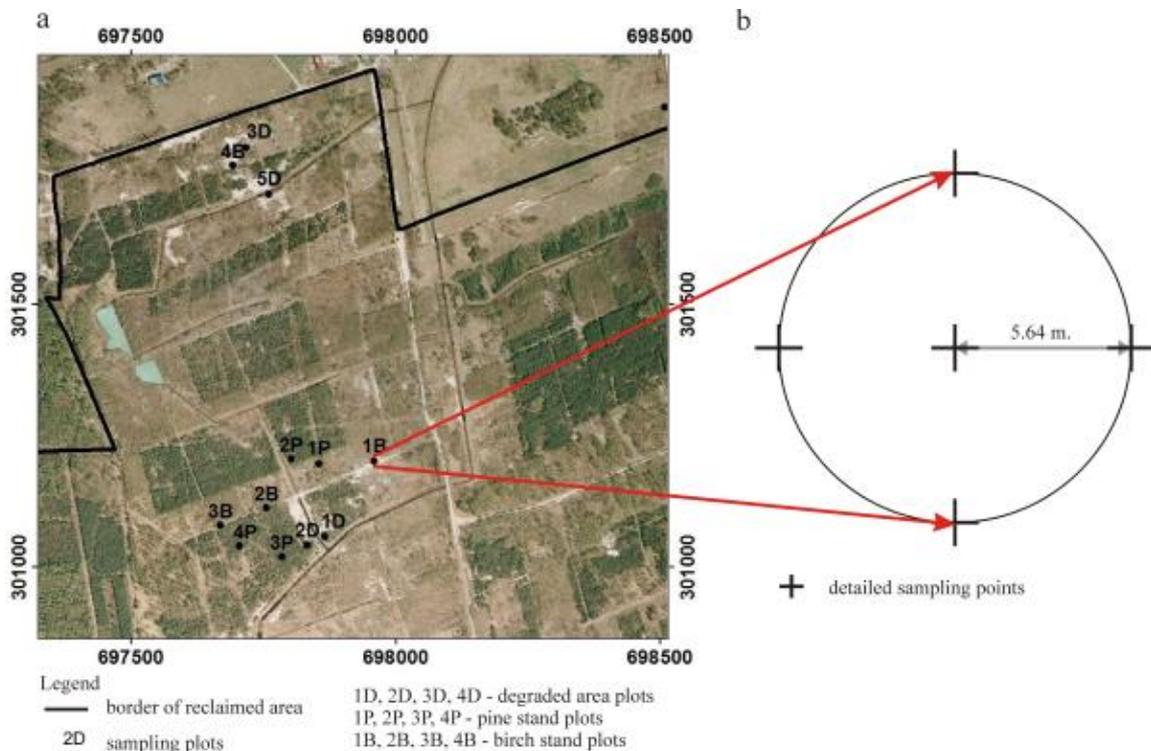
Figure 6. Examples of sampling points.

Assessment of soil and vegetation on detailed points

After determining land cover classes (orthophoto screen vectorization in the ArcMap ArcGIS 10.2, ESRI, Redlands, CA, USA), detailed sample plots were selected in three categories (Fig. 7 a), i.e.:

- P, B category - effectively reclaimed and forested site category (pine P and birch B stands, 4 plots each);
- D category - degraded category with no plants or little surface coverage with herbaceous vegetation or trees (4 plots).

Soil samples were collected on 1-ar ($r = 5.64$ m) circular surfaces from 0-20 cm, 20-50, and 50-100 cm horizon. Five points arranged in a regular pattern - one point in the middle



and four 5.64 m from the inside in the north, east, south, and west toward (Fig. 7 b).

Figure 7. Distribution of research sites in designated categories (a), the arrangement of 5 soil sampling points on 1-ar ($r = 5.64$ m) circular surfaces (b); (Likus-Ciešlik et al., 2015).

The pH, EC, S_T , SOC, and N_T were analyzed in the samples according to the methodology given above on samples of DP. Additionally, on the 1-ar sites, the degree of herbaceous plant coverage was determined according to the Braun-Blanquet scale and species, tree crown cover was determined; diameter at breast height (DBH) and height (H_i) of trees were measured.

Vegetation chemistry

Samples to assess the chemistry of foliage and mineral nutrition of plants were collected from sites in previously defined categories (D, P, B). 1-year-old or current year needle (P_c) and 2-year-old (P_{c+}) Scots pine needles and common birch leaves were collected from P and B category plots. Also leaf of wood small-reed (*Calamagrostis epigejos* (L.) Roth) were collected. Wood small-reed was the species that appeared on every research plot. The

concentration of macroelements N, S in plant samples was determined using a Leco TruMac (Leco Corporation, Saint Joseph, MI, USA) and the concentration of K, P, Ca, Mg, and K after mineralization in a mixture of HNO₃ and HClO₄ (ratio of 3: 1) was determined on the ICP OES ICAP 6000 Series spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA).

Sulfur leaching and biogeochemical transformation

Biogeochemical transformations of mineral sulfur in the soil environment were researched in 12 weeks of the experiment under controlled conditions. There was used soil substrate (collected in the post-mining site in D category) in two variants of sulfur contamination: low sulfur concentrate substrate (LS) – average 5,090 mg·kg⁻¹ S and high sulfur concentrate substrate (HS) – average 42,500 mg·kg⁻¹ S). Additionally, in the experiment litterfall collected from birch (B) and pine (P) stands (managed stands to eliminate the impact of sulfur from the mine), were used to test the inhibitory impact of organic matter to rate of mineral sulfur transformation. From air-dried substrate (5 cm thickness) and litter samples (20 g) composites were created in the following combinations (four replications each):

- LS-B and LS-P – substrate with low sulfur concentration + birch or pine litter, respectively;
- HS-B and HS-P – substrate with high sulfur concentration + birch or pine litter;
- control composite with no litter LS-c, HS-c.

At the beginning of the experiment, in the soil samples grain size, pH, EC, S_t, SOC, N_t, Ca, Mg, and Al concentration was determined. In the litter samples pH, S_t, N_t, C, Ca, Mg, and Al was determined and C:N ratio was calculated. After 12 weeks of the experiment, the properties of the used substrates and litter were analyzed again (the same properties as at the beginning of the experiment beside grain size). During 12 weeks of the experiment the soil-litter composites (Fig. 8) were rinsed with 100 ml of distilled water twice a week and once a week water filtrate was collected to determine pH, EC, dissolved organic carbon (DOC), N_t, Ca, Mg, Al, and S_t.

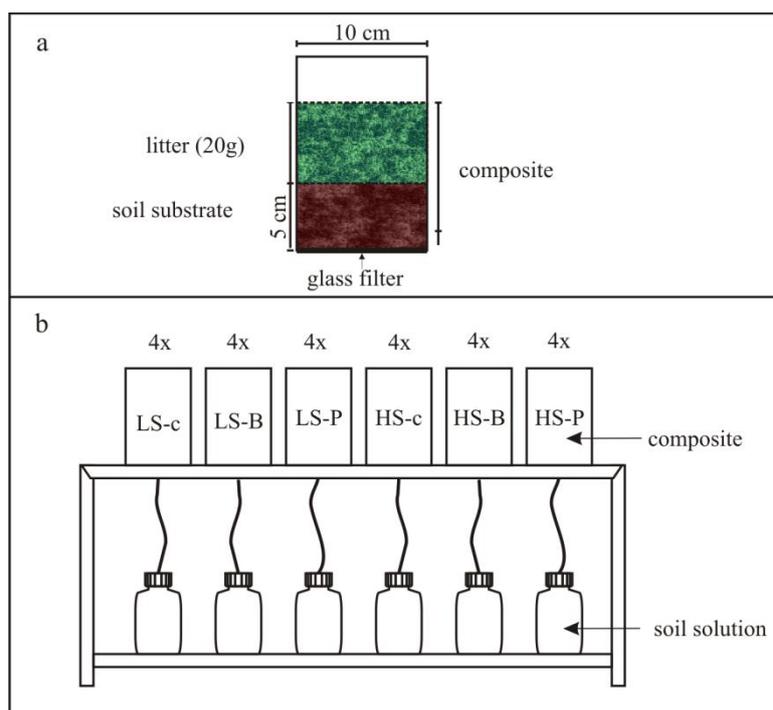


Figure 8. Composite scheme (a), and general scheme of experiment with a varied composition (b); (Likus-Cieřlik et al., 2018).

Results

The assessment of sulfur distribution and contamination

Soil pH_{KCl} on the FJSM area ranged from 2.6 to 7.6 (Table 1, Fig. 9 a). Fourth-nine percent of sampling points had acidic pH (pH_{KCl} from 2.7 to 6.5). The soil EC values were not alarming and ranged from 15 to 2,080 $\mu\text{S}\cdot\text{cm}^{-1}$ (Table 1, Fig. 9). Only at two points, the EC value was exceeded at 2,000 $\mu\text{S}\cdot\text{cm}^{-1}$ (according to the FAO guidelines; Abrol et al., 1988). EC above 2,000 $\mu\text{S}\cdot\text{cm}^{-1}$ is considered as an amount at which the growth and yield of sensitive plants may be limited. The sulfur concentration in the topsoil horizons ranged from 10 to 45,740 $\text{mg}\cdot\text{kg}^{-1}$ (Table 1). The natural concentration of sulfur (according to the Institute of Crop and Soil Fertilization guidelines; (Kabata-Pendias et al., 1995) was characterized by 35% of the analyzed area. High concentration (slight contamination) and very high concentration (heavy contamination) of sulfur were reported on 12% and 26% of the researched area respectively, (Fig. 9c).

The scale of high sulfur concentration is not large (hot-spots occurred on 2% of the researched area). The most contaminated sites concentrated mainly in the northern and central parts of the site.

Table 1. Selected topsoil (0-20 cm) characteristics on reclaimed sites at the FSMJ as grouped by soil texture (Likus-Cieślak et al., 2017).

	Soil texture			pH _{KCl}	EC μS·cm ⁻¹	S _T mg·kg ⁻¹	
	USDA	Sand	Silt %				Clay
Mean (range)	S	91	7	2	5.1 (3.3-7.6)	92 (16-314)	212 (10-1099)
SD					1.6	101	322
Mean (range)	LS	77	19	4	4.4 (2.6-7.5)	222 (15-1573)	2185 (0-25575)
SD					1.8	425	6584
Mean (range)	SL	67	27	6	5.6 (2.8-7.5)	412 (21-2080)	5002 (10-40805)
SD					1.9	653	11221
Mean (range)	L	47	43	10	6.5 (3.8-7.3)	1332 (27-2000)	15388 (56-27930)
SD					1.5	833	11985
Mean (range)	SiL	28	55	14	7.0 (6.8-7.1)	1625 (1212-1940)	35731 (32096-45742)
SD					0.2	308	6688

Explanations: USDA – U.S. Department of Agriculture; LS – loamy and; S – sand; SL – sandy loam; L – loam; SiL – silt loam (according to USDA) EC – electrical conductivity; S_T – total soil sulfur, SD – standard deviation values in brackets indicate ranges.

Surface water chemistry

The surface water pH ranged from 2.6 to 7.9 (Table 2). However, the lowest pH occurred only in points 2, 3, and 10 (hot-spot; pH from 2.6 to 3.1; Fig. 5). The average electrolytic conductivity was 1,797 μS·cm⁻¹ (from 1,083 to 3,430 μS·cm⁻¹, Table 2). According to the current legal standards in Poland (RME, 2016) high EC (i.e., EC > 1500 μS·cm⁻¹) indicating salinity of waters was found in 82% of the analyzed samples. Extremely high values of EC were noted in point No 10 (Figure 5). SO₄²⁻ concentration was very high and ranged from 472 to 1503 mg·L⁻¹ (Table 2). Also Ca²⁺ ion concentration was high, an average was 332,37 mg·L⁻¹ (from 174.5 to 433.9). The concentration of the remaining ions in the surface waters of the investigated site was relatively low (Table 2) and had no impact on the reduction of the overall chemical quality assessment.

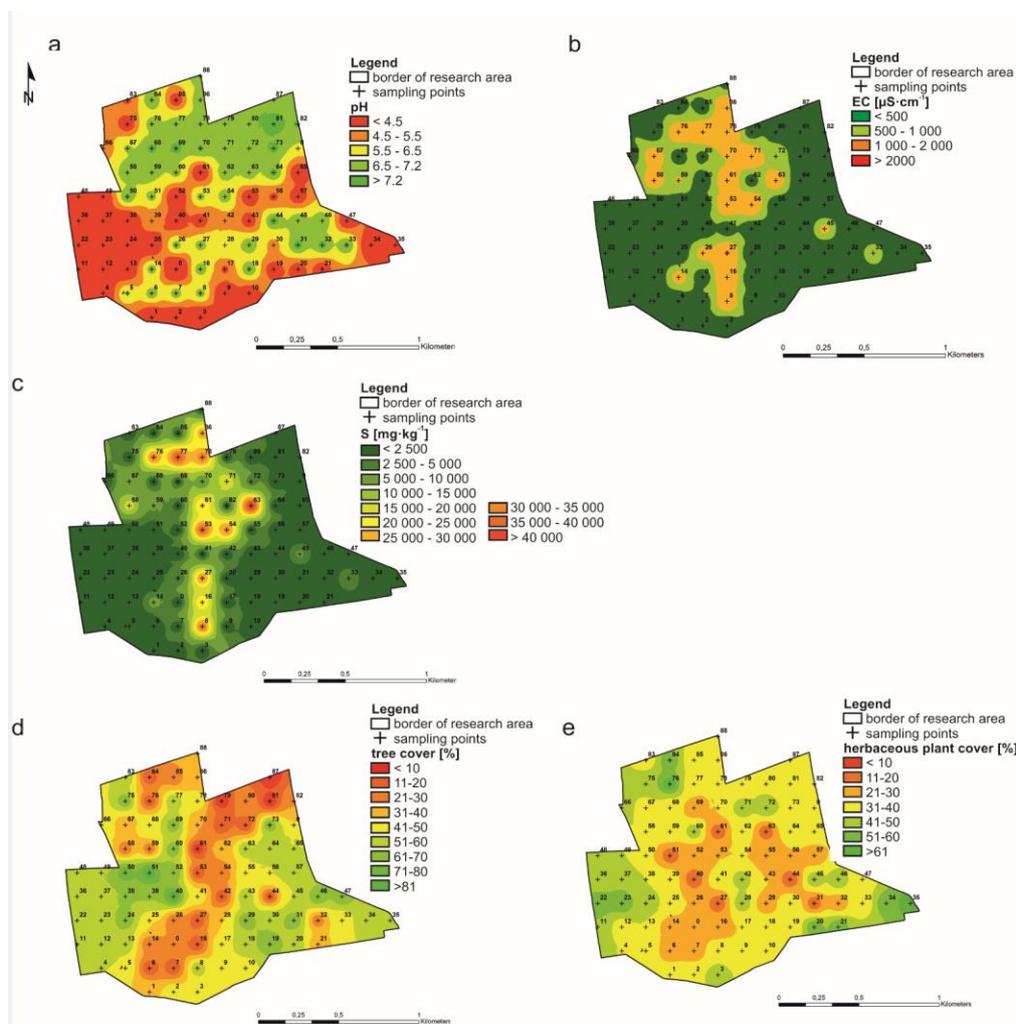


Figure 9. Spatial distribution pH (a), EC (b), S_T (c), tree cover (d), herbaceous vegetation cover (e) on the reclaimed FSMJ site (Likus-Cieřlik et al., 2017).

Table 2. Average values and the range of pH, EC, and concentration of selected ions in researched seasons in the reclaimed and afforested areas of FSMJ (Likus-Cieřlik et al., 2019).

Sampling season	pH	EC $\mu\text{S}\cdot\text{cm}^{-1}$	SO_4^{2-}	Ca^{2+} $\text{mg}\cdot\text{L}^{-1}$
Summer	6.5 (3.1-7.7) †	1819 (1660-2070)	1049.4 (829.5-1321.9)	358.3 (276.3-405.8)
Autumn	6.6 (3.4-7.7)	1823 (1720 -2120)	994.5 (593.8-1312.2)	343.0 (197.9-406.7)
Winter	6.2 (2,7-7,2)	1823 (1083-2190)	742.5 (472.0-988.1)	285.4 (174.5-390.6)
Spring	6,7 (2,6-7,9)	1980 (1118-3430)	954.1 (500.2-1502.9)	342.75 (222.3-433.9)

† 6.5 (3.1-7.7) – mean (range); bdl – below detection level

Assessment of soil and vegetation on detailed points

Areas classified as degraded (D) were characterized by high sulfur contamination ($>23,000 \text{ mg}\cdot\text{kg}^{-1}$), acidic pH (from 2.7 in 50-100cm horizon to 3.9 in 0-20 cm horizon), and high salinity ($\text{EC} >1600 \mu\text{S}\cdot\text{cm}^{-1}$). The soils also displayed a low concentration of organic carbon and nitrogen (SOC and N_T , Table 3). Such unfavorable soil properties lead to significant forest growth inhibition or even dieback. The trees from D were characterized by the worst parameters: the average number of trees/ha (N) was 612, the DBH 7.7 cm, and the height H_t 5.5 m compared to P and B category (Table 4). In D category conditions, there is significant inhibition of vascular plant succession (surface coverage by herbaceous vegetation on average 26%, Table 4 Category). D surfaces are an example of inefficient reclamation, especially acidity neutralization and sulfur contamination isolation that played a key role in the reclamation process. Surfaces classified as properly reclaimed and afforested (P and B) had a lower soil sulfur concentration (from 274.87 to 1891.72 $\text{mg}\cdot\text{kg}^{-1}$ in P, from 7891.63 to 17609.83 $\text{mg}\cdot\text{kg}^{-1}$ in B; Table 3). Soil pH in P and B categories was also higher than D (from 4.6 to 6.0 in P, from 4.2 to 6.7 in B; Table 3).

Table 3. Selected soil characteristics (detailed areas) in the reclaimed and afforested areas of FSMJ (Likus-Cieřlik et al., 2015).

Cat.	Soil horizon cm	pH_{KCl}	EC $\mu\text{S}\cdot\text{cm}^{-1}$	S_T $\text{mg}\cdot\text{kg}^{-1}$	SOC %	N_T
B [†]	0-20	6.7±1.3	707±1132	17609.8±57883	1.8±1.3	0.05±0.04
	20-50	5±1,2	421±653	12717.8±36221	0.6±1.0	0.01±0.02
	50-100	4.2±1.8	564±658	7891.6±16631	0.9±0.7	0.03±0.03
P	0-20	6.0±1.7	369±480	1891.7±5388	1.5±0.8	0.06±0.03
	20-50	4.6±1.1	347±469	978.8±3284	0.8±0.8	0.03±0.03
	50-100	5.2±1.1	296±262	274.9±223	0.6±0.4	0.02±0.01
D	0-20	3.9±1.8	1840±1220	24569.7±37249	1.4±1.2	0.03±0.02
	20-50	3.3±1.4	1860±1410	23775.1±43725	1.1±0.9	0.02±0.02
	50-100	2.7±0.9	1612±967	89326.4±107323	1.1±0.8	0.03±0.03

[†] B – birch stands category, P – pine stands, D – degraded

Vegetation chemistry

Based on data from an analysis of dry needle weight it was found that the highest sulfur concentration (S) was found in birch leaves (mean 1,954 $\text{mg}\cdot\text{kg}^{-1}$). S concentration in P_c was 1,272 $\text{mg}\cdot\text{kg}^{-1}$, in one-year-old pine needle P_{c+1} 1,221 $\text{mg}\cdot\text{kg}^{-1}$. Significant differences were found in S concentration between the species (Table 5). Based on data it may be concluded that tree supply with nutrients Ca (birch B 1.35%, pine P_c 0.33%, P_{c+1} 0.75%), Mg (B 1526 $\text{mg}\cdot\text{kg}^{-1}$, P_c 705 $\text{mg}\cdot\text{kg}^{-1}$, P_{c+1} 715 $\text{mg}\cdot\text{kg}^{-1}$), K (B 0.80%, pine P_c 0.50%, P_{c+1} 0.50%);

Table 5) is suitable while N (B 1.71%, P_c 1.12%, P_{c+1} 1.11%; Table 5) is a deficit nutrient for the trees occurring in the investigated areas.

Table 4. Selected characteristics of tree and vegetation in the reclaimed areas of FSMJ (Likus-Ciešlik et al., 2015).

Category	N t.	DBH cm	Ht m	IUFRO			Number of vascular plant species pcs/plot	Cover abundance of vegetation %
				10	20	30		
D	612 (238-1090) [†]	7.7 (5.0-10.04)	5.5 (3.61-6.88)	7	40	53	10 (1-16)	26 (1-55)
P	1457 (1051-2133)	10.6 (9.17-11.53)	10 (9.54-10.63)	25	63	12	14 (8-21)	35 (3-75)
B	1558 (637-2038)	7.8 (5.67-8.89)	8.3 (6.1-11.35)	9	70	21	14 (12-19)	74 (60-85)

[†]Mean (range)

Table 5. The supply of macronutrients and S to birch and pine foliage (broken down into needles from 2 age groups) in sulfurous FSMJ soils (Likus-Ciešlik, Pietrzykowski, 2017).

Category [†] and research material ^{††}		N	P	Ca	Mg	K	S	N:P
		%	mg·kg ⁻¹	%	mg·kg ⁻¹	%	mg·kg ⁻¹	
B	median (mean)	1.68* (1.71)	2309.3* (2320.4)	1.30* (1.35)	1494.9* (1525.7)	0.72* (0.80)	1987* (1954)	7.6
	range	1.58-1.89	1695.8- 2969.3	1.15-1.63	1039.9- 2073.1	0.68-1.07	1218- 2626	
	median (mean)	1.07** (1.12)	1358.3** (1348.1)	0.32** (0.33)	705.2** (705.2)	0.49** (0.50)	1287** (1272)	
P _c	range	1.05-1.30	1221.3- 1454.3	0.25-0.44	645.0- 765.5	0.46-0.56	1054- 1459	
	median (mean)	1.10** (1.11)	1049.6** (1045.4)	0.78*** (0.75)	710.6** (715.0)	0.49** (0.50)	1208** (1221)	10.6
P _{c+1}	range	1.05-1.81	970.6- 1111.8	0.52-0.93	687.5- 751.5	0.48-0.53	955- 1513	

[†]B – birch stand category, P – pine, D – degraded, ^{††}P_c – current year needles, P_{c+1} – two-year-old pine needles, *, **, *** – significant at the 0.05 probability level between categories, bdl – below detection level

In the above-ground parts of *Calamagrostis epigejos* was found a deficit of N and P (mean N 0.62%, mean P 904 mg·kg⁻¹ in cat. D; mean N 0.93%, mean P 1,351 mg·kg⁻¹ in cat. P; mean N 0.75 mg·kg⁻¹, mean P 1,132 mg·kg⁻¹ in cat. B; Table 6).

The highest concentration of sulfur in *Calamagrostis epigejos* was on P category (2,249 mg·kg⁻¹). In B category mean S was 1,717 mg·kg⁻¹ and in D 1,778 mg·kg⁻¹ (Table 6). It was surprising that in the most sulfurized soil category (D) higher amounts of this element were not reported in above-ground tissue parts of the plant compared to afforested areas which displayed lower sulfur concentration in the soil.

Table 6. Nutrient concentration and N:P ratio in wood small-reed leaves in defined categories in reforested FSMJ areas (Likus-Cieślak and Pietrzykowski, 2017).

Category [†]		S mg·kg ⁻¹	N %	P mg·kg ⁻¹	K %	Ca %	Mg mg·kg ⁻¹	N:P
P	mean	2249.*	0.93* (0.97)	1351.2* (1381.1)	0.95* (0.87)	0.34* (0.33)	706.* (644.1)	6.9
	(median)	(2262.8)						
	range	2087.8- 2383.0	0.71-1.09	1235.3-1407.3	0.82-1.25	0.20-0.50	603.4-932.5	
B	mean	1717.3*	0.75*, ** (0.73)	1132.5* (1182.3)	0.72* (0.76)	0.27* (0.31)	485.5*, ** (506.1)	6.7
	(median)	(1689.1)						
	range	1406.6- 2084.4	0.56-0.99	749.2-1416.3	0.37-0.98	0.15-0.33	296.8-633.1	
D	mean	1778.5*	0.62** (0.67)	904* (739.3)	0.57* (0.57)	0.22* (0.24)	363.9** (390.6)	7.7
	(median)	(2042.4)						
	range	790.6- 2238.5	0.40-0.72	519.3-1618.3	0.23-0.91	0.09-0.28	175.1-499.5	

[†]B – birch stand category, P – pine, D – degraded; *, **, *** – significant at the 0.05 probability level between categories

Sulfur leaching and biogeochemical transformation

The results of the experiment indicate that the rate and the amount of leached elements depended firstly on the amount of sulfur in the substrate (LS or HS). At the beginning of experiment S concentration was HS 42,521 mg·kg⁻¹, LS 5090 mg·kg⁻¹ (Table 7). After 12 weeks of the experiment, there was a significant reduction in sulfur concentration in the composites with highly sulfated HS solely due to rinsing them (HS-c 35,634 mg·kg⁻¹, HS-B 33,247 mg·kg⁻¹, HS-P 34,157 mg·kg⁻¹; Table 7). However, the level of S concentration is still very high. In less sulfated variant (LS) rinsing of substrates has a significant impact on a reduction of EC in the substrate (LS 1.87 mS·cm⁻¹, LS-c 0.39 mS·cm⁻¹, LS-B 0.59 mS·cm⁻¹, LS-P 0.23 mS·cm⁻¹; Table 7). It was shown that pine litter has a significant impact on increasing the pH of the soil substrate (LS-B 2.1, LS-P 2.9, Table 7), however, the pH of the substrates was still toxic (below 3; Table 7).

The basal respiration rate (RESP) values were extremely low for HS-c and LS-c substrates (control) as well as for treated samples (with litter; Table 7). The application of litter did not affect respiration activity.

Birch litter had an impact on more leaching of N_t from HS and of Mg from both substrates (Table 8). At the beginning of the experiment N_t in birch litter was higher (17.20 g·kg⁻¹) than pine litter (6.45 g·kg⁻¹; table 8), so the leaching of N_t was higher in composites with the birch litter addition. Increased leaching of N_t, Mg was observed in both substrates. The rate of DOC leaching influenced by litter was connected to its type (Table 9).

Table 7. Chemical parameter changes of soil-substrate during a 12-week experiment under controlled conditions (Likus-Cieřlik et al., 2018).

Properties		LS [†]		LS-c		LS-B		LS-P	
pH		2.1 ^{a††} ± 0.0 [‡]	2.6 ^{bc} ± 0.0	2.5 ^{bd} ± 0.1	2.9 ^e ± 0.3				
EC	mS cm ⁻¹	1.87 ^a ± 0.06	0.39 ^b ± 0.03	0.59 ^c ± 0.11	0.23 ^d ± 0.23				
St	mg kg ⁻¹	5090 ^a ± 483	6447 ^a ± 397	5947 ^a ± 1319	6178 ^a ± 1870				
SOC		3.22 ^a ± 0.09	2.89 ^a ± 0.32	2.97 ^a ± 0.16	3.09 ^a ± 0.20				
Nt		0.03 ^a ± 0.03	0.02 ^a ± 0.01	0.03 ^a ± 0.01	0.02 ^a ± 0.00				
Ca	g·kg ⁻¹	7.06 ^a ± 0.5	0.07 ^b ± 0.1	0.06 ^b ± 0.0	0.38 ^b ± 0.4				
Mg		0.09 ^a ± 0.01	0.04 ^b ± 0.01	0.04 ^b ± 0.00	0.05 ^b ± 0.00				
Al		0.97 ^{ab} ± 0.09	0.37 ^c ± 0.25	0.43 ^c ± 0.03	0.49 ^c ± 0.04				
RESP	$\mu\text{g CO}_2/\text{g}/24\text{h}$	n.d. ^{†††}	2.49 ^a ± 0.5	2.75 ^a ± 1.4	1.91 ^a ± 0.7				
		HS		HS-c		HS-B		HS-P	
pH		2.5 ^{bc} ± 0.0	2.6 ^c ± 0.0	2.3 ^d ± 0.0	2.5 ^{bc} ± 0.1				
EC	mS cm ⁻¹	2.59 ^e ± 0.05	2.53 ^e ± 0.08	2.98 ^f ± 0.12	2.58 ^e ± 0.05				
St	mg kg ⁻¹	42521 ^b ± 2670	35634 ^c ± 9568	33247 ^c ± 4033	34157 ^c ± 4291				
SOC		7.78 ^b ± 0.13	7.23 ^b ± 0.34	7.80 ^b ± 1.14	7.20 ^b ± 0.44				
Nt		0.16 ^b ± 0.02	0.19 ^{bc} ± 0.04	0.22 ^c ± 0.04	0.18 ^b ± 0.01				
Ca	g·kg ⁻¹	11.68 ^c ± 1.6	4.21 ^{de} ± 2.3	2.95 ^d ± 0.7	5.99 ^{de} ± 2.2				
Mg		0.11 ^a ± 0.00	0.08 ^c ± 0.04	0.11 ^a ± 0.01	0.11 ^a ± 0.01				
Al		1.51 ^e ± 0.00	0.77 ^{ad} ± 0.44	1.02 ^{ab} ± 0.18	1.25 ^{be} ± 0.17				
RESP	$\mu\text{g CO}_2/\text{g}/24\text{h}$	n.d.	2.40 ^a ± 0.6	0.99 ^a ± 0.5	2.24 ^a ± 0.6				

[†]LS – soil substrate with 5,090 mg·kg⁻¹ S before the experiment; LS-c – control sample of soil substrate with 5,090 mg·kg⁻¹ S after the experiment; LS-B birch litter after the experiment on substrate with 5,090 mg·kg⁻¹ S; LS-P – pine litter after the experiment on substrate with 5,090 mg·kg⁻¹ S; HS-b – soil substrate with 42,500 mg·kg⁻¹ S before the experiment; HS-c – control sample of soil substrate with 42,500 mg·kg⁻¹ S after the experiment; HS-B – birch litter after the experiment on substrate with 42,500 mg·kg⁻¹ S; HS-P – pine litter after the experiment on substrate with 42,500 mg·kg⁻¹ S; ^{††}a,b – mean values with the same letter are not significantly different at p=0.5, 2.53±0.04 – mean and SD; ^{†††}n.d. – no data.

Table 8. Changes in birch and pine litter chemical parameters during a 12-week experiment under controlled conditions.

Properties		B [†]	LS-B	HS-B	P	LS-P	HS-P
pH		5.3 ^a ±0.1 [‡]	5.8 ^b ±0.2	5.2 ^a ±0.3	4.2 ^c ±0.0	5.6 ^d ±0.1	5.4 ^{ad} ±0.1
St	mg·kg ⁻¹	1415 ^a ±29	1913 ^a ±380	5236 ^b ±1388	877 ^a ±40	1301 ^a ±266	4386 ^b ±1215
C		476 ^{ac} ±12	415 ^b ±46	414 ^b ±24	500 ^c ±2	428 ^b ±50	439 ^{ab} ±23
N _t	g·kg ⁻¹	17.2 ^a ±0.2	18.9 ^b ±2.2	18.73 ^{ab} ±1.0	6.5 ^c ±0.4	6.0 ^c ±0.8	6.4 ^c ±0.2
Ca		8.4 ^a ±0.3	14.5 ^b ±2.2	14.2 ^b ±1.9	14.6 ^b ±0.2	9.0 ^{ac} ±0.4	10.3 ^c ±0.7
Mg		0.5 ^a ±0.0	0.9 ^{bc} ±0.1	0.8 ^b ±0.1	1.0 ^c ±0.0	0.5 ^a ±0.0	0.5 ^a ±0.0
Al		0.1 ^a ±0.0	0.6 ^b ±0.3	0.6 ^b ±0.3	0.2 ^a ±0.0	0.3 ^a ±0.1	0.4 ^{ab} ±0.2
C:N		28 ^a	22 ^b	22 ^b	77 ^c	68 ^d	71 ^d
RESP	μg CO ₂ /g/24h	n.d. [§]	1736 ^{bc} ±195	1506 ^c ±549	n.d.	2926 ^a ±370	2340 ^{ab} ±329

[†]B – birch litter before the experiment; **LS-B** – birch litter after the experiment on substrate with 5,090 mg·kg⁻¹ S; **HS-B** – birch litter after the experiment on substrate with 42,500 mg·kg⁻¹ S; **P** – birch litter before the experiment; **LS-P** – pine litter after the experiment on substrate with 5,090 mg·kg⁻¹ S; **HS-P** – pine litter after the experiment on substrate with 42,500 mg·kg⁻¹ S; [§]n.d. – no data; [‡]a,b – mean values with the same letter are not significantly different at p=0.5, 2.53±0.04 – mean and SD.

Table 9. Mean values and standard deviations for pH, EC, the concentration of dissolved organic carbon (DOC) and the concentrations of St, Nt, Ca, Mg and Al in leachates at the beginning and after 12 weeks of leaching through soil substrates and composites in controlled conditions (Likus-Cieślak et al., 2018).

		LS-c	LS-B	LS-P	HS-c	HS-B	HS-P
pH	s [†]	1.8 ^{b†††} ±0.0	1.8 ^b ±0.0	1.8 ^b ±0.1	2.2 ^b ±0.0	2.2±0.1	2.3 ^b ±0.1
	f ^{††}	2.5 ^a ±0.1	2.8 ^a ±0.1	3.8 ^a ±0.3	2.6 ^a ±0.2	2.2±0.2	2.9 ^a ±0.3
EC mS·cm ⁻¹	s	10.80 ^a ±1.4	11.48 ^a ±0.4	10.91 ^a ±3.1	4.85 ^a ±0.3	5.52±0.8	4.51 ^a ±0.5
	f	1.12 ^b ±0.3	0.71 ^b ±0.2	0.10 ^b ±0.0	2.74 ^b ±0.3	4.75±1.0	2.40 ^b ±0.4
St mg·kg ⁻¹	s	1570.8 ^a ±157	1585.9 ^a ±100	1583.3 ^a ±427	814.3 ^a ±31	841.4±74	741.0 ^a ±74
	f	71.0 ^b ±20	53.7 ^b ±17	9.6 ^b ±5	625.7 ^b ±37	725.4±64	588.0 ^b ±24
DOC mg·l ⁻¹	s	82.8 ^a ±9	93.0 ^a ±9	117.1 ^a ±19	101.4 ^a ±10	127.0 ^a ±33	110.4 ^a ±15
	f	5.1 ^b ±0	20.5 ^b ±3	37.2 ^b ±11	9.8 ^b ±2	32.0 ^b ±4	29.6 ^b ±3
Nt mg·l ⁻¹	s	14.7 ^a ±2.0	18.1 ^a ±1.0	16.4 ^a ±4.1	5.7 ^a ±0.3	7.7 ^a ±1.6	6.5 ^a ±0.7
	f	0.5 ^b ±0.0	1.5 ^b ±0.2	1.2 ^b ±0.3	0.4 ^b ±0.0	2.6 ^b ±0.7	0.8 ^b ±0.1
Ca mg·l ⁻¹	s	474.4 ^a ±39	445.3 ^a ±26	442.8 ^a ±33	550.2 ^a ±18	552.8 ^a ±14	553.4±50
	f	5.8 ^b ±1	13.7 ^b ±4	5.2 ^b ±6	467.3 ^b ±24	494.8 ^b ±22	495.6±17
Mg mg·l ⁻¹	s	2.2 ^a ±1.7	7.9 ^a ±1.5	8.0 ^a ±3.1	0.0 ^c ±0.0	1.6 ^{ad} ±1.0	0.9 ^d ±1.7
	f	0.0 ^b ±0.0	0.7 ^b ±0.1	0.1 ^b ±0.1	0.0 ^c ±0.0	2.2 ^a ±0.5	0.5 ^d ±0.1
Al mg l ⁻¹	s	73.2 ^a ±12	61.2 ^a ±7	60.7 ^a ±25	43.0 ^a ±6	32.4 ^a ±11	21.7 ^a ±9
	f	0.2 ^b ±0.2	0.1 ^b ±0.0	0.1 ^b ±0.0	0.7 ^b ±0.4	1.8 ^b ±0.5	0.2 ^b ±0.1

[†]s – at the beginning of experiment; ^{††}f – after 12 weeks; ^{†††}different letters indicate significant differences in the measured values at the beginning and at the end of the experiment (p=0.05, pairwise t-test)

Discussion

According to other authors (Kabata-Pendias et al., 1995, Stevenson and Cole, 1999), the sulfur concentration in natural and non-contaminated soil ranges from 100 to 1000 mg·kg⁻¹. According to Contaminated Sites Regulation by Environmental Management Act of Canada (EMA, 1996) the level of S concentration in agricultural soils cannot exceed 500 mg kg⁻¹ of S in soil. In the researched area, sulfur (32,000 to 45,000 mg·kg⁻¹ on degraded D area) concentration can be considered very high concentration of S on FSMJ was exceeded even 90-fold according to EMA (1996), and 45-fold according to Kabata-Pendias et al., (1995) and Stevenson and Cole (1999). Degraded areas covered a small area (4.39 ha) compared to the researched area (above 200 ha). It may seem little, but these areas represent the uniqueness of the worldwide scale reconstructed biochemical system and are important for the research about plant reactions to environmental stress, especially excessive sulfur concentration.

Not only places where sulfur was excavated are connected with high sulfur concentration in soil. Alberta in Canada (a sour gas processing plant) is an example of a high contaminated place by sulfur (S concentration in soil was from 500 to 6,000 mg kg⁻¹). Sulfurous soil occurred also in a former coal mining site like LuzatiaRegion (coal contained up to 3% of S; Katzur and Haubold-Rosar 1996).

In FSMJ, there were no significant correlations between soil sulfur concentration and soil acidification because of neutralization treatment with flotation lime during the reclamation process. For example on the FSMJ points exist where sulfur exceeds 2,500 mg kg⁻¹ (what is considered by very high concentration) and pH was over 7.0 (alkaline) (Likus-Cieřlik et al., 2017). In a natural condition, high sulfur concentration in soil is connected with low (acidic) pH (Benson, Bowen, 2013). Sulfur concentration in the topsoil also had no relation to vegetation cover and abundance, and it proved impossible to determine the direct toxic effect of sulfur concentration on vegetation.

The chemistry of surface water had quite good parameters (mostly high pH, around 7, but there were places where pH was low in each sampling season). Among the analyzed elements, increased content was observed in the case of SO₄²⁻ and Ca ions. The concentration of sulfate ions in individual research seasons was 4 to up to 12-fold higher than defined in the current standards (RME, 2016) for good quality waters (i.e., SO₄²⁻ < 138.5 mg·L⁻¹). Water chemistry was related to the specific geochemical system of the anthropogenically transformed environment: high SO₄²⁻ ion concentration was related to high

soil sulfation, and high Ca^{2+} ion concentration was due to using sludge lime for neutralization. Because of high sulfate concentration and local hotspots with a low pH indicate an AMD, surface water in FSMJ should be monitored.

The concentration of biogenic elements in the foliage of the investigated tree species is within the range provided by ICP-Forest (Stefan et al., 2002) as an excellent element concentration (Likus-Cieřlik, Pietrzykowski 2017). With regard to the nutrition of pine and birch trees in industrialized regions (Heinsdorf, 1999), tree supply with nitrogen in the investigated former sulfur mine sites was exceedingly low for the pine (supply grade 1) and low for the birch (supply grade 2). Phosphorus ($\text{B } 2320 \text{ mg}\cdot\text{kg}^{-1}$, $\text{P}_c 1348 \text{ mg}\cdot\text{kg}^{-1}$, $\text{P}_{c+1} 1045 \text{ mg}\cdot\text{kg}^{-1}$; Table 5), K and Mg concentration in foliage on FSMJ was sufficient or good. In assessing forest tree stand nutrition it is also important to examine the proportions between macronutrients, especially the N to P ratio (Baule and Fricker, 1973). The N:P ratio in pine needles ranged from 7.6 (in birch leaves), to 10.6 (P_{c+1}) (Likus-Cieřlik and Pietrzykowski, 2017). The N:P ratio in pine needles obtained by Pietrzykowski et al., (2013) in the former opencast Piaseczno sulfur mine was 10. Pietrzykowski et al., (2013) found no significant differences between the N:P in mine land and the control (managed stands in natural habitats). The results obtained in FJSM yielded similar values as in the Piaseczno and “natural” stands. It may be thought that supply in a biogenic element is rather good.

According to the Holub et al., (2012) *Calamagrostis epigejos* is a plant which has been found highly tolerant to abiotic stress factors. *Calamagrostis epigejos* is a dominant species in Central European post-mining lands at an initial successional stage (Mudrak et al., 2010). We also found that *Calamagrostis epigejos* is tolerant to high S concentration in the soil.

The obtained results of the experiment indicated that the addition of organic matter, especially in the case of the most sulfur-contaminated soil, is not sufficient for detoxification. It may be assumed that under the impact of decomposing organic matter and biochemical processes, there will be more intensive leaching and migration of macroelements deep into the soil profile followed by soil development. However, in the conditions of the most heavily sulfated soils without neutralization, this will be a very long process. To decrease the negative effects of excessive sulfur concentration in soil, the use of lime (limestone, hydrated lime, quick lime) is recommended (EPA 2007). McTee (2017) reported that CaCO_3 application was the most efficient way to improve an ecological properties of acidic soils contaminated with elemental sulfur. Although pH of the substrates increased over 12 weeks

of the experiment, it was still within the range of toxic values and soil pH was found to be the major factor affecting soil microorganisms (Rousk et al., 2010).

Conclusions

Despite of the reclamation treatment, in the studied area there are still hotspots of very high concentrations of sulfur in the soil (even up to 45000 mg·kg⁻¹), low pH (<2.0), and electrical conductivity (EC) reaches even 2080 μS·cm⁻¹. The hotspots cover a relatively small area (about 2%) of the monitored surface (216.5 ha), but it was shown to be a significant soil disturbance affecting the undesirable reaction of vegetation. Also, surface waters were characterized by good chemical parameters (average pH 6.5), however, there were points with low pH (from 2.6 to 3.1) and high SO₄²⁻ (average 935.13 mg·L⁻¹) concentration. In this case, it seems to be important, that the area should be monitored because of the risk of acid mine drainage (AMD).

The growth of trees on afforested areas (B and P categories) indicated that after careful acidity neutralization, the growth of herbaceous plants and trees were characterized by relatively good growth parameters and viability. *Calamagrostis epigejos* turned out to be a high tolerance species to high sulfur concentration in soil, even on extremely sulfated soils (D category). *Calamagrostis epigejos* could be used in the natural succession of similar sites as alternative temporary biological stabilization.

The results of the experiment under controlled conditions indicated that organic matter addition affects the dynamics of the soil solution, but does not affect the increase of mineral sulfur leaching. The effect of sulfur is only the result of the rinsing substrates - the organic matter had no influence to change of sulfur in soil solution. A significant reduction of sulfur concentration in the substrate as a result of rinsing will take place in the contaminated environment for a long time, and without full neutralization of acidity the soil detoxification effect will not be achieved.

Acknowledgements

The study was financed by Polish Ministry of Science and Higher Education within the framework of 2016-2018 Statutory Funds (DS ZEKLiR 3420, and BM 4444, BM 4544).

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