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Comprehensive Study of Soil-Plant and Surface Water Chemistry Relationships in Highly S Contaminated Environment on Reforested Former Sulfur Borehole Mine Sites

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Abstract: Sulfur contamination of topsoil, spatial distribution of contamination and surface water chemistry were investigated on an area of over 200 ha of a new forest ecosystem. Common birch and Scots pine growth reaction, vitality and nutrients supply, as well as wood small-reed (Calamagrostis epigejos (L.) Roth) chemical composition were assayed. The chemistry dynamics of soil leaching and the sulfur load leached from the sulfur contaminated soil-substrates were analyzed. The remediation effect of the birch and pine litter was assayed in an experiment under controlled conditions. It was found that reclamation was effective in a majority of the post-mining site, however hot-spots with sulfur contamination reaching even 45,000 mg kg^{-1}, pH <2.0, and EC 6,500 μS cm^{-1} were reported. Surface waters typically displayed elevated concentrations of sulfate ions (average 935.13 mg L^{-1}), calcium ions (up to 434 mg L^{-1}) and high EC (average 1.795 μS cm^{-1}), which was connected both with sulfur contamination and sludge lime used in neutralization. Wood small-reed was found to be species adapting well to the conditions of elevated soil salinity and sulfur concentration. We noted that an addition of organic matter had a significant impact on the chemistry of soil solutions but did not indicate in short term experiment a remediation effect by increased sulfur leaching.

Keywords: sulfur; reclamation; acid mine drainage; salinity; soil contamination

1. Introduction

Currently, Poland is the only country where native sulfur is extracted on a large scale. In 2015, 627.6 thousand Mg sulfur was mined [1,2]. Sulfur deposits occur in southern Poland, in the Tarnobrzeg area (Osiek, Baranów, Machów, Jeziórko deposits), Staszów (Solec and Grzybów deposits) and Lubaczów (Basznia field) [2]. Sulfur deposits were extracted first in the sixties of the twentieth century with the open strip mining method (Piaseczno Mine and Machów Mine), and then using the borehole Frasch's method [3,4]. 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. Subsequently, sulfur is melted underground and it is pumped to the surface in liquid form [5]. This method was used in Poland in the following mines: Grzybów (1966-1996), Basznia (1977-1993), Machów II (1985-1993), Jeziórko (1967-2001), and around the world in mines in the USA (until 2000) and Iraq (until 2003) [6]. Currently, the Frasch method is used in Osiek Mine in Poland (since 1993) and in Mexico (since 2010) [6, 7].

Reclamation of sulfur-bearing sites, in particular ones mined using the Frasch process, is very difficult and complex as it leads to significant and multifactorial transformations of the environment including chemical contamination with sulfur, acidification, geomechanical deformations of the earth's surface in the form of subsidence, hydrological changes in the form of flooding events, changes in the direction of watercourses, acid mine drainage (AMD) [3]). A characteristic feature of the distribution of contaminated sites and soil acidification in the areas mined using the Frasch process is the occurrence of hotspots resulting from numerous liquid sulfur leakages due to borehole and pipeline technological problems (transmission installations, [4]). Furthermore, in post-mining sites, liquefied sulfur spilt in an uncontrolled manner from technological storage sites heavily contaminating adjacent areas [8].

In spite of reclamation requiring considerable technical involvement carried out in post-mining areas, the remaining dispersed hotspots became an example of microhabitats with excessive sulfur concentration, constituting new conditions for animal, vegetation and microorganisms. Thus research conducted in such sites provides a unique opportunity learn about the response and the rate of forest ecosystem restoration, including an assessment of trees and herbaceous plant reactions to environmental stress with strong soil and water sulfur contamination.

The aim of the work was to comprehensively study of soils, surface waters and reactions of trees and herbaceous plants in the restored forest ecosystem on the former sulfur mine, based on collected preliminary study results. Soil contamination and plant reactions were analyzed both spatially in a network of monitoring points covering over 200 ha of reclaimed land as well as in reductionist approach on study plots representing various categories of ecosystem degradation. The chemistry of surface water was also analyzed as an indispensable element of the restored ecosystem in spatial and seasonal variations. The results were supplemented by a simulation of the rate of sulfur leaching from soils and changes in soil solution chemistry in the leaching experiment conducted under controlled conditions.

2. Materials and Methods

2.1. *Study site*

The study was conducted on reclaimed and reforested mining areas of the former Jeziórko sulfur mine (FSMJ) (Southern Poland, 50º32’34 N, 21º47’46 E) (Figure 1). The region has an average annual temperature of +8.2 °C (–1.6 °C in January, and +18.7 °C in July) and average annual precipitation ranges from 550 to 650 mm. The growing season lasts from 200 to 220 days per annum.

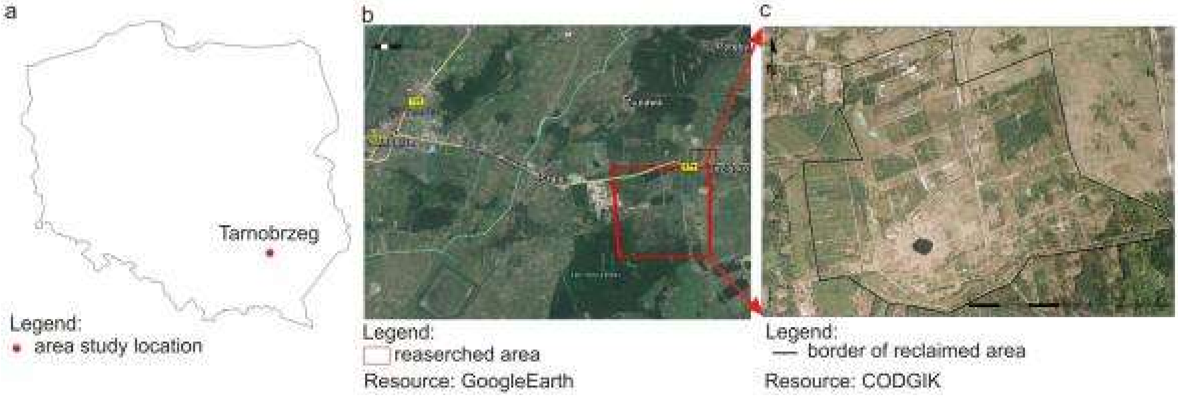

Figure 1. Research area location on map of Poland (a) and reclaimed and reforested area border (b and c).

Reclamation treatments of FSMJ area started in 1993. 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 State Forest National Forest Holding (Figure 1b). Reclamation treatment included 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} of sludge lime), fertilization (70 kg ha^{-1} P_2O_5, 60 kg ha^{-1} K_2O), and sowing of grass seeds [4]. 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.,) [3].

2.2. *Field and laboratory study*

As part of field work, a total of 88 sampling points were located in the FSMJ area in a regular grid of squares with sides measuring 150 m (Figure 2). The sampling points were first identified on the map using ArcGIS software (ESRI), and then targeted and stabilized using the Garmin GPS receiver (GPSMAP® 60CSx).

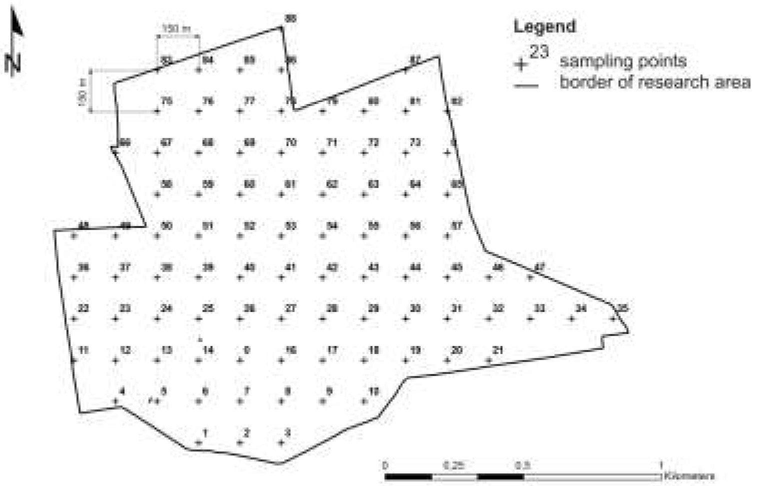

Figure 2. Distribution of sampling points on reclaimed and afforested the FSMJ site.

At the monitoring points, soil samples were taken from the top layer (0-20 cm). In the laboratory the collected soil samples were analyzed for grain size using the Fritsch GmbH Laser Particle Sizer ANALYSETTE 22, 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). Soil organic Carbon SOC, total Nitrogen N_T, total Sulfur S_T were measured with the TruMac Leco CNS analyzer. 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 (IUNG, Poland) [9].

Samples of surface water were collected from 15 monitoring points on reservoirs and watercourses (Figure 3) in the summer, autumn, winter and spring. The water sampling were analyzed for pH, EC and ionic content (Ca^{2+} Mg^{2+}, Na^{+}, NO^{3-}, SO_4^{2-}, Cl^{-}, HCO^{3-}) on the Dionex Ion Chromatography 5000 apparatus. The spatial variability of ionic content and hydrogeochemical classification was assessed according to Szczukariew-Prikłoński classification.

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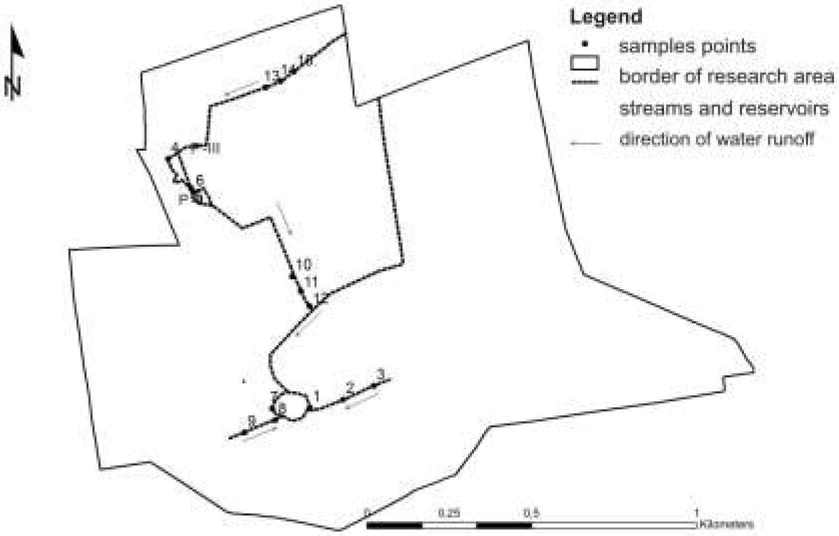

Figure 3. Distribution of surface water sampling points from watercourse reservoir in reclaimed and afforested FSMJ area.

Based on dGPS measurements, the exact position of research sites was determined and data was collected to make a photointerpreting key (geotagging of photographs). After determining land cover classes (orthophoto screen vectorization in the ArcMap ArcGIS 10.2, Esri program), patches of microhabitats were selected in three categories (Figure 4), i.e.: effectively reclaimed and forested site category (pine P and birch B stands, 4 plots each) and degraded D stand with little surface coverage with herbaceous vegetation and occasional trees from natural succession (4 plots). Detailed research were carried out on 1-ar (r = 5.64 m) circular study plots from which composite soil samples were collected from 0-5 cm and 5-40 cm horizon (samplig was conducted in five points arranged in a regular pattern - one point in the middle and four in the corners of the square inscribed in the circular study plots). Than pH, EC, S_T, SOC and N_T were analyzed in the samples, according to the standard methodology (given previously). The degree of herbaceous plant coverage on study plots was determined according to the Braun-Blanquet's scale and an inventory of existing trees were made. For trees DBH and height Ht were measured.

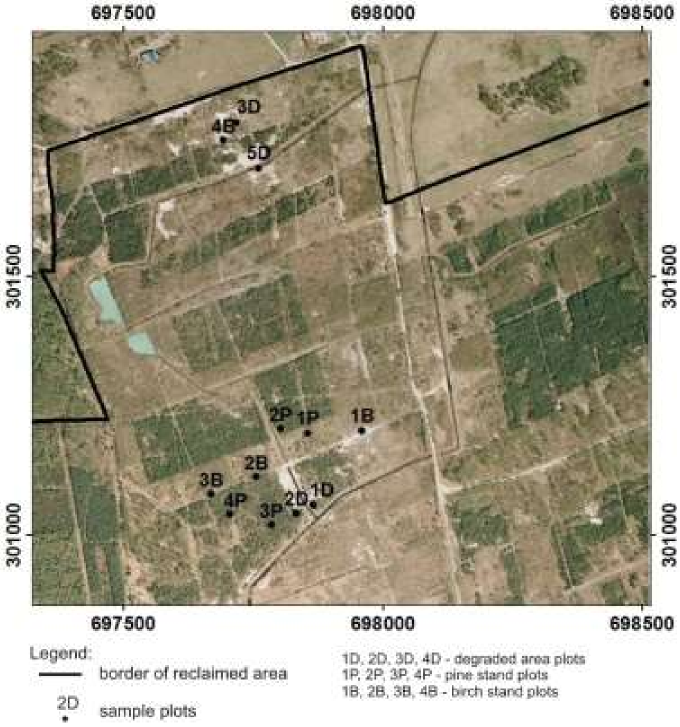

Figure 4. Distribution of detailed study sites (after first phase of surface variability study in the monitoring grid) with designated categories.

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Samples for the chemistry of foliage and nutrient supplying assessment of plants were collected from sites in previously defined categories (D, P, B), including 1-year-old (current year P_c) and 2-year-old (P_{c+1}) Scots pine needles and silver birch leaves. Foliage samples were collected from trees top (SW exposition) growing on reclaimed and reforested sites (pine and birch stands, i.e. P and B category plots). Also mixed samples (one per each plot) of wood small-reed leaf (*Calamagrostis epigejos* (L.) Roth) were collected. The reason was because It was an undergrowth species that appeared on each research plot. The content of N and S in plant tissue samples were determined on Leco TruMac while the other macroelements (Na, K, P, Ca, Mg and K) were determined after mineralization in a mixture of HNO_3 and $HClO_4$ (in ratio of 3: 1) on the ICP OES ICAP 6000 Series spectrophotometer.

Spatial imaging (map compositions, Figure 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 [10].

Using the Statistica 12 software [11], correlations between the concentration of ST sulfur in topsoil horizons and pH, EC and vegetation surface coverage were investigated. The correlation between soil chemistry and plant macronutrient supply was also studied using the ANOVA test and Pearson correlation.

As part of studies on biogeochemical transformations of mineral sulfur and soil dissolution chemistry changes in the highly contaminated environment the experiment under controlled conditions was designed, taking into account the possible inhibitory impact of organic matter in the form of litterfall collected from birch and pine stands. We designed two different variants of soil substrate sulfur contamination: LS - average 5,090 mg kg^{-1} S and HS – 42,500 mg kg^{-1} S). in habitat conditions. At the beginning of the experiment, the input (starting) properties of the substrates prepared and used in the experiment were determined (soils: grain size, pH, EC, S^T, SOC, N^T, Ca and Mg content, litter: pH, S, N, C, Ca and Mg content the C:N ratio was calculated. Soil material was collected in the post-mining site (substrates from plots in the previously described D category - degraded [3]. Litterfall was collected from managed stands to eliminate the impact of sulfur from the mine. In the course of the experiment the soil-litter composites 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 and S. After the experiment, the properties of the used substrates and litter were analyzed again (substrate: pH, EC, S_T, SOC, N_T, Ca and Mg content; litter: pH, S, N, C, Ca and Mg content, C:N ratio was calculated).

3. Results

3.1. Soil pH and contamination spatial variability

Soil pH_{KCl} varied from 2.6 to 7.6 (Table 1, Figure 5 a). Sampling points with acidic pH (pH_{KCl} from 2.7 to 6.5) constituted 49%, with neutral pH (pH_{KCl} from 6.6 to 7.2) 38%, and with alkaline pH (pH_{KCl}> 7.3) 13% of the study area. The soil EC ranged from 15 to 2,080 µS cm^{-1} (Table 1, Figure 5 b). Only at two monitoring points, the EC value was exceeded at 2,000 µS cm^{-1}, which according to the FAO guidelines [12] means that growth of sensitive plants may be limited. The sulfur content in the topsoil layers was from 10 to 45,740 mg kg^{-1} (Table 1). Sulfur content, similar to the natural content according to IUNG guidelines [9] was found on 35% of the analyzed site. According to these guidelines elevated S content was noted on 28%, high S content (slight contamination) on 12%, and very high content (heavy S contamination) on 26% (Figure 5c). Extreme sulfur concentrations exceeded more than 10-fold the highest degree in IUNG scale. Sulfur concentration (S_T) positively correlated with EC (r = 0.80) and pH (r = 0.42). In some spots, extremely contaminated with sulfur, there was more than 30% herbaceous plant coverage (3 and 4 on the Braun-Blanquet scale).

Table 1. Selected topsoil layer (0-20 cm) characteristics on the FSMJ area, as grouped by soil texture [4].

	USDA	sand	silt	clay	pH_{KCl}	EC	N_T	SOC	S_T
				[%]		[µS cm^{-1}]	[%]	[%]	[mg kg^{-1}]
Mean	S	91	7	1	5.12 (3.30-7.59)	92 (16-314)	0.02 (0.00-0.08)	0.57 (0.12-1.87)	212 (10-1099)
SD					1.58	101	0.02	0.47	322
Mean	LS	77	19	4	4.43 (2.62-7.51)	222 (15-1573)	0.11 (0.00-0.41)	2.59 (0.25-10.68)	2185 (0-25575)
SD					1.79	425	0.14	3.10	6584
Mean	SL	67	27	6	5.57 (2.75-7.49)	412 (21-2080)	0.08 (0.00-0.39)	2.28 (0.69-8.15)	5002 (10-40805)
SD					1.89	653	0.09	1.86	11221
Mean	L	47	43	10	6.46 (3.83-7.27)	1332 (27-2000)	0.03 (0.01-0.06)	3.67 (0.95-7.58)	15388 (56-27930)
SD					1.47	833	0.02	2.43	11985
Mean	SiL	28	55	14	7.00 (6.79-7.13)	1625	0.02 (0.00-0.05)	5.42 (2.76-6.76)	35731 (32096-45742)
SD					0.16	308	0.02	1.88	6688

Explanations: LS – loamy sand; S – sand; SL – sandy loam; L – loam; SiL – silt loam (according to USDA 2014)EC – electrical conductivity; N_T – total nitrogen; SOC – soil organic carbon; S_T – total soil sulfur, SD – standard deviation values in brackets indicate ranges.

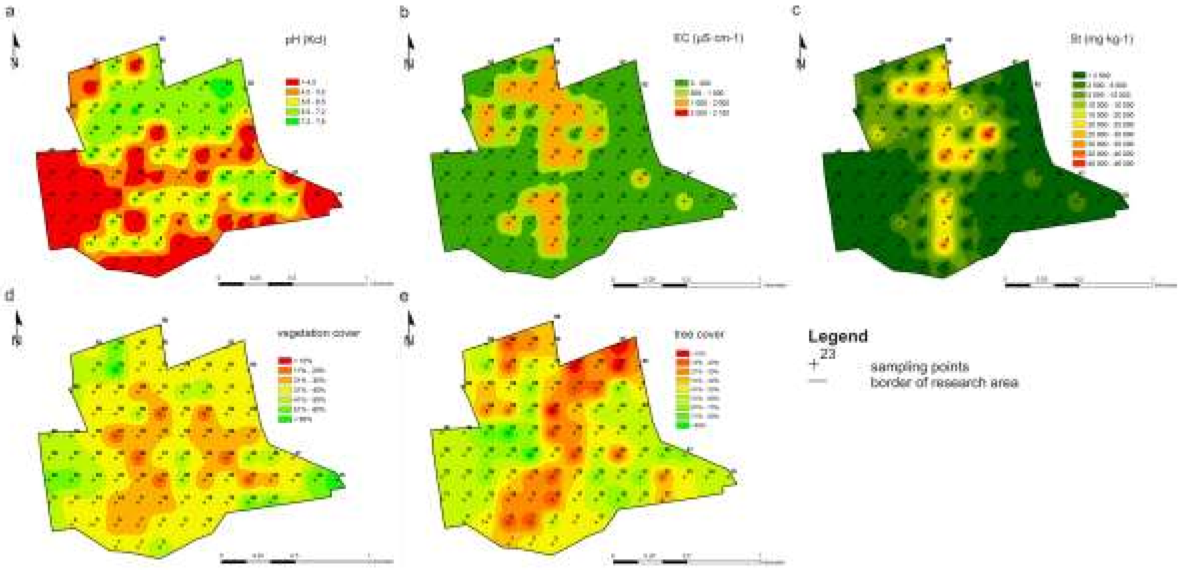

Figure 5. Spatial distribution of pH (a), EC (b), S_T (c), tree cover (d), herbaceous vegetation cover (e) on the studied FSMJ area [4].

High sulfur concentration in the soil did not lead to strong acidification due to neutralization with high doses of sludge lime. However, with sulfur high concentration in soil samples, high EC and limited vegetation were reported, which could be considered as a good bioindicator of ineffective reclamation.

However places with high sulfur contamination were considered as hotspots, the scale of the phenomenon is not large, and the distribution of contamination of the topsoil is irregular and dispersed. The most contaminated sites concentrated mainly in the northern and central parts of the studied site.

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3.2 Surface water chemistry variability

The average water pH value range, calculated on whole database ranged from pH 2.6 to 7.9 (Table 2). In the monitored site hot spots were noted with extreme low pH values, ranged from 2.6 to 3.1. Differences in pH between the studied seasons were not significant. The average electrical conductivity EC for the entire investigated period was 1,797 $\mu S\ cm^{-1}$, and ranged from 1,083 to 3,430 $\mu S\ cm^{-1}$, Table 2). According to the legal standards [13] high EC (i.e. EC > 1500 $\mu S\ cm^{-1}$) indicating salinity of waters, so we noted in this category 82% of the analyzed samples. SO_4^{2-} content ranged from 472 to 1503 mg L^{-1} (Table 2). The concentration of sulfate ions in seasonal variability was 4 to up to 12-fold higher than defined in the current standards [13] for good quality waters (i.e.$SO_4^{2-}<138.5$ mg L^{-1}). Thus, generally, water mineralization in the studied site was high. The average total mineralization for the entire monitoring period was 1,489 mg L^{-1}. Sulfate ions (63%) and calcium ions (22%) accounted for the largest share. High SO_4^{2-} ion content was related to high soil sulfation, while increased Ca^{2+} ion concentration was due to applying doses of sludge lime for neutralization in the course of site reclaim treatments. In conclusion the problem for the investigated surface waters was mainly the outcome of extremely low pH recorded at some points, high EC and high SO_4^{2-} concentration. 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 overall water chemical quality assessment.

Table 2. pH, EC and concentration of selected ions in during the sampled seasons in the FSMJ study sites [8].

	Season			
	Summer	Autumn	Winter	Spring
pH	6.5 (3.1-7.7)	6.6 (3.4-7.7)	6.2 (2,7-7,2)	6,7 (2,6-7,9)
		$\mu S\ cm^{-1}$		
EC	1819 (1660-2070)	1823 (1720 -2120)	1823 (1083-2190)	1980 (1118-3430)
		mg L^{-1}		
Cl^-	76.83 (11.2-113.2)	75.87 (9.5-122.4)	67.42 (7.5-110.0)	73.14 (7.2-123.7)
HCO_3^-	8.63 (1.8-13.7)	9.92 (2.4-15.6)	bdl	78.33 (8.5-131.0)
NO_3^-	1.00 (0.4-3.4)	1.24 (0.4-2.7)	1.86 (0.4-6.9)	bdl
SO_4^{2-}	1049.39 (829.5-1321.9)	994.52 (593.8-1312.2)	742.48 (472.0-988.1)	954.11 (500.2-1502.9)
Na^+	97.61 (22.5-134.9)	96.82 (24.0-145.7)	79.47 (13.7-122.9)	93.87 (11.2-147.1)
Mg^{2+}	21.44 (16.0-29.1)	21.09 (14.4-30.8)	15.83 (8.2-22.0)	23.11 (14.3-30.8)
Ca^{2+}	358.32 (276.3-405.8)	343.00 (197.9-406.7)	285.40 (174.5-390.6)	342.75 (222.3-433.9)

[1] 6.5 (3.1-7.7) – mean (range); bdl – below detection level

However, studied water is not natural deep mineral waters but rather extensively anthropogenically transformed surface waters, in which SO_4^{2-} and Ca^{2+} ions determined the chemistry. According to Szczukariew-Prikłoński hydrogeochemical classification studied waters were mainly sulfate-calcium classes (58%). Water chemistry was directly related to the specific geochemical system of anthropogenically transformed environment due to sulfation caused by borehole sulfur extraction and by liming in the course of technical reclamation.

3.3. *Soil and vegetation relationships*

It was confirmed that areas classified as degraded (D) typically displayed high sulfur contamination, i.e. from 50 to 28,900 mg kg^{-1}, acidic pH (pH$_{KCl}$ from 1.9 to 6.5) and high salinity (EC from 149 to 1160 μS cm^{-1}, Table 3). The soils also displayed a low content 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 density, i.e. the average number of trees ha^{-1} (N) was 612, the DBH 7.7 cm and the height H$_t$ 5.5 m (Table 4). In these conditions, there is a 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 in term of neutralization and isolation of highly S contaminated layers. Surfaces classified as successfully reclaimed and reforested (cat. P and B) had a lower soil sulfur concentration. In P category, sulfur concentration in the soil ranged from 10 to 1,200 mg kg^{-1} (Table 3), while in B category from 90 to even 5,300 mg kg^{-1} (Table 3). Soil pH in these categories was also higher than in category D, though it also varied widely from 3.9 to 7.1 and from 4.5 to 6.6 in category P and in category B, respectively (Table 4). In category P and B sites significantly more trees with apparently better growth parameters were reported, in comparison to category D, where trees were rare and deformed (Table 3).

It should be emphasized, however, that D category covered a small total area of 4.39 ha in the entire facility. This, of course, compared to hundreds of hectares of land reclaimed effectively may seem little, but on the other hand these areas represent the extreme site conditions for plants, microorganisms and animal and uniqueness of the reconstructed biochemical system studies.

Table 3. Selected soil characteristics (detailed areas) in the reclaimed and afforested areas of FSMJ [3].

Category	Soil horizon	pH$_{KCl}$	EC μS cm^{-1}	S$_T$ Mg kg^{-1}	SOC %	N$_T$
B	0-20	6.7±1.3	707±1132	17609.83±57882.88	1.8±1.32	0.05±0.04
	20-50	5±1,2	421±653	12717.75±36221.24	0.6±1.02	0.01±0.02
	50-100	4.2±1.8	564±658	7891.63±16631.18	0.87±0.7	0.03±0.03
P	0-20	6.0±1.7	369±480	1891.72±5388.58	1.5±0.83	0.06±0.03
	20-50	4.6±1.1	347±469	978.8±3284.43	0.76±0.76	0.03±0.03
	50-100	5.2±1.1	296±262	274.87±223	0.63±0.44	0.02±0.01
D	0-20	3.9±1.8	1840±1220	24569.68±37249.22	1.39±1.15	0.03±0.02
	20-50	3.3±1.4	1860±1410	23775.14±43725.62	1.11±0.89	0.02±0.02
	50-100	2.7±0.9	1612±967	89326.42±107323.19	1.06±0.79	0.03±0.03

D – degraded, P – pine stands, B – birch stands

Table 4. Selected characteristics of tree and vegetation in the reclaimed areas of FSMJ [3].

Category	N [pcs ha^{-1}]	DBH [cm]	Ht [m]	V [m^3 ar^{-1}]	IUFRO 10 [%]	20	30	Number of vascular [pcs plot^{-1}]	Cover abundance [%]
D	612	7.7	5.5	0.06	7	40	53	10 (1-16)	26 (1-55)
P	1457	10.6	10	0.93	25	63	12	14 (8-21)	35 (3-75)
B	1558	7.8	8.3	0.50	9	70	21	14 (12-19)	74 (60-85)

Mean (range)

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3.4. *Foliage chemistry and macronutrient supply*

Macronutrient supply to trees in the reclaimed post-mining sites were generally adequate, i.e. within the ranges determined by ICP-Forest [14]. Mean phosphorus content (P) in birch foliage was 2,320.4 mg kg^{-1}, and in pine needles in (P_c) the mean was 1,348.1 mg kg^{-1}, whereas in older needles (P_{c+1}) the mean was 1,045.4 mg kg^{-1}. Mean potassium content (K) in birch leaves was 0.80%, and in pine needles in P_c the mean was 0.50%, in P_{c+1} the man was 0.50%, respectively (Table 5). Mean calcium content (Ca) in birch leaves was 1.35%, and in pine needles in P_c the mean was 0.33%, in P_{c+1} the mean was 0.75%, respectively (Table 5). Mean magnesium content (Mg) in birch leaves was 1,526 mg kg^{-1} and in pine needles in P_c the mean was 705 mg kg^{-1}, in P_{c+1} the mean was 715 mg kg^{-1}, respectively. Mean sodium content (Na) in birch leaves was 34.9 mg kg^{-1}, and in pine needles in P_c the mean was 10.3 mg kg^{-1}, in P_{c+1} the mean was 10.0 mg kg^{-1}, respectively (Table 5). Significant differences were found in P, K, Ca, Mg and Na content between the birch and the pine while differences between needle age were found only in the case of Ca (Table 5).

Table 5. The supply of S and other macronutrients in birch and pine foliage on sulfurous FSMJ soils [7].

			Foliage species[1],[2]		
			B	P	
Element				P_c	P_{c+1}
N	[%]	mean (median)	1.71^{a} (1.68)	1.12^{b} (1.07)	1.11^{b} (1.10)
		range	1.58-1.89	1.05-1.30	1.05-1.81
P	[mg kg^{-1}]	mean (median)	2320.4^{a} (2309.3)	1348.1^{b} (1358.3)	1045.4^{b} (1049.6)
		range	1695.8-2969.3	1221.3-1454.3	970.6-1111.8
Ca	[%]	mean (median)	1.35^{a} (1.30)	0.33^{b} (0.32)	0.75^{c} (0.78)
		range	1.15-1.63	0.25-0.44	0.52-0.93
Mg	[mg kg^{-1}]	mean (median)	1525.7^{a} (1494.9)	705.2^{b} (705.2)	715.0^{b} (710.6)
		range	1039.9-2073.1	645.0-765.5	687.5-751.5
K	[%]	mean (median)	0.80^{a} (0.72)	0.50^{b} (0.49)	0.50^{b} (0.49)
		range	0.68-1.07	0.46-0.56	0.48-0.53
Na	[mg kg^{-1}]	mean (median)	34.9^{a} (37.1)	10.3^{b} (11.0)	10.0^{b} (8.5)
		range	17.46-47.88	bdl. – 19.1	1.3-21.74
S	[mg kg^{-1}]	mean (median)	1954^{a}(1987)	1272^{b}(1287)	1221^{b}(1208)
		range	1218-2626	1054-1459	955-1513

[1] B – leaves of birch growing in category of birch stands, P – pine needles, and category; [2] P_c – current year needles, P_{c+1} – two-year-old pine needles, ^{a,b} – significant difference between categories , bdl – below detection level; category D - lack of trees

The highest sulfur content (S) was found in birch leaves (mean 1,954 mg kg^{-1}). S content in pine needles P_c was 1,272 mg kg^{-1}, and in P_{c+1} 1,221 mg kg^{-1}. Significant differences were found in S content between the species (Table 5).

Nitrogen content, as a deficient nutrient in these conditions, was 1.71% in birch leaves and in 1.12% and 1.11 % in pine needles, respectively for P_c and P_{c+1} it.

In the above-ground parts of wood small-reed, there was noted a deficit of nitrogen, as well, and phosphorus (mean N 0.62%, mean P 904 mg kg^{-1} in category 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). In category D, no elevated S

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content was found in wood small-reed tissue (1,779 mg kg^{-1}) compared to other categories (2,249 mg kg^{-1} P, 1,717 mg kg^{-1} B, Table 6).

Table 6. Nutrient content and N:P ratio in wood small-reed leaves at different degree of degraded site categories in reforested FSMJ areas [7].

		Category[1]		
		P	B	D
		%		
N	mean (median)	0.93^{a} (0.97)	0.75^{ab} (0.73)	0.62^{b} (0.67)
	Range	0.71-1.09	0.56-0.99	0.40-0.72
K	mean (median)	0.95^{a} (0.87)	0.72^{a} (0.76)	0.57^{a} (0.57)
	Range	0.82-1.25	0.37-0.98	0.23-0.91
Ca	mean (median)	0.34^{a} (0.33)	0.27^{a} (0.31)	0.22^{a} (0.24)
	Range	0.20-0.50	0.15-0.33	0.09-0.28
		mg kg^{-1}		
S	mean (median)	2249.1^{a} (2262.8)	1717.3^{a} (1689.1)	1778.5^{a} (2042.4)
	Range	2087.8-2383.0	1406.6-2084.4	790.6-2238.5
P	mean (median)	1351.2^{a} (1381.1)	1132.5^{a} (1182.3)	904^{a} (739.3)
	Range	1235.3-1407.3	749.2-1416.3	519.3-1618.3
Mg	mean (median)	706.1^{a} (644.1)	485.5^{ab} (506.1)	363.9^{b} (390.6)
	Range	603.4-932.5	296.8-633.1	175.1-499.5
Na	mean (median)	25.0^{a} (15.8)	22.2^{a} (22.4)	11.3^{a} (5.9)
	Range	13.6-54.7	13.3-30.4	4.2-29.3
N:P ratio	mean (median)	6.9	6.7	7.7

[1] B – birch stand category, P – pine stand category, D – degraded category, ^{a,b} – significant difference between categories (at p= 0.05)

Sulfur content in tree foliage correlated positively with sulfur content in the soil (r = 0.61) and with EC (r = 0.68) and negatively with nitrogen content in the soil N (r = -0.66). In the case of wood small-reed on all plots in site categories, linear correlations between the mentioned features did not occur. It was found that wood small-reed probably applied a strategy based on the mechanism of blocking the uptake of sulfur from the highly contaminated soil. It is definitely a species resistant to the existing conditions of environmental stress and sulfurous soils. Thus, we recognized that wood small-reed, as a succession species, has a beneficial phytostabilizing impact and may be used in remediation of such type of soils.

3.5. *Chemistry of soil solution in the leaching experiment under controlled conditions*

However it was easy predictable that the rate and amount of leached elements depended firstly on amount of sulfur in the substrate (LS or HS), 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 42.521 mg kg^{-1}, HS-c 35,634 mg kg^{-1}, HS-B 33,247 mg kg^{-1}, HS-P 34,157 mg kg^{-1}, Table 7). It was observed that despite a significant reduction in S_t content in composites with highly sulfated substrate (HS), the level of sulfation is still very high and exceeds the values provided by IUNG standards (the Institute of Crop and Soil Fertilization) as very high sulfur content (strongly contamination), i.e. above 1,000 mg kg^{-1} [9] up to 35-fold. The results of the experiment in a less sulfated variant (LS) indicate that the rinsing of substrates has a significant impact on a big reduction

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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 phytotoxic (pH below 3.0). Low soil-substrate pH during litter decay is a normal phenomenon in natural conditions, because organic acids are released causing a drop in soil pH [15].

Table 7. Chemical parameter changes of soil-substrate during a 12-week experiment under controlled conditions [16].

Properties		**LS**^{1}	**LS-c**	**LS-B**	**LS-P**	**HS**	**HS-c**	**HS-B**	**HS-P**
pH		2.1^{a} ± 0.0‡	2.6^{bc} ± 0.0	2.5^{b} ± 0.1	2.9^{e} ± 0.3	2.5^{bc} ± 0.0	2.6^{c} ± 0.0	2.3^{d} ± 0.0	2.5^{bc} ± 0.1
EC	[mS	1.87^{a} ± 0.05	0.39 ± 0.03	0.59 ± 0.1	0.23 ± 0.2	2.59^{e} ± 0.05	2.53^{e} ± 0.07	2.98^{f} ± 0.12	2.58^{e} ± 0.04
St	[mg kg^{-1}]	5090 ± 483	644 ± 397	594 ± 131	617 ± 187	4252 ± 267	3563 ± 956	3324 ± 403	3415 ± 429
SO		3.22^{a} ± 0.09	2.89 ± 0.32	2.97 ± 0.1	3.09 ± 0.2	7.78^{b} ± 0.13	7.23^{b} ± 0.34	7.80^{b} ± 1.14	7.20^{b} ± 0.44
Nt		0.03^{a} ± 0.03	0.02 ± 0.01	0.03 ± 0.0	0.02 ± 0.0	0.16^{b} ± 0.02	0.19^{b} ± 0.04	0.22^{c} ± 0.04	0.18^{b} ± 0.01
Ca	[g kg^{-1}]	7.06^{a} ± 0.50	0.07 ± 0.05	0.06 ± 0.0	0.38 ± 0.3	11.68 ± 1.56	4.21^{d} ± 2.25	2.95^{d} ± 0.73	5.99^{d} ± 2.23
Mg		0.09 ± 0.01	0.04 ± 0.01	0.04 ± 0.0	0.05 ± 0.0	0.11^{a} ± 0.00	0.08^{c} ± 0.04	0.11^{a} ± 0.01	0.11^{a} ± 0.01
Al		0.97^{a} ± 0.09	0.37 ± 0.25	0.43 ± 0.0	0.49 0.0	1.51^{e} ± 0.00	0.77^{a} ± 0.44	1.02^{a} ± 0.18	1.25^{b} ± 0.17
RES	[µg	n.d.	2.49 ± 0.48	2.75 ± 1.3	1.91 ± 0.7	n.d.	2.40^{a} ± 0.57	0.99^{a} ± 0.48	2.24^{a} ± 0.59

^{1}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 42500 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; ^{2}a,b – mean values with the same letter are not significantly different at p=0.5, 2.53±0.04 – mean and SD; ^{3}n.d. – no data.

It was found that birch litter had an impact on stronger leaching of N$_{t}$ from HS and of Mg from both substrates (Table 8). At the beginning of the experiment birch litter was richer in N$_{t}$ than pine litter, therefore the leaching of this element was higher in the case of composites with the addition of birch litter. In the experiment with rinsing of technogenic soil substrates with the addition of litter in controlled conditions, Woś and Pietrzykowski [17] reported a significant impact of birch litter on the intensification of soil-forming processes and increased leaching of DOC, N$_{t}$ and Mg. A similar tendency was observed in the case of N$_{t}$ and Mg in both substrates, but it was found that the rate of DOC leaching is influenced by litter, regardless of its type. Menyailo [18] found that some species impact a change in soil pH, DOC and Mg, but they did not observe the differences by impact of individual species on the content of Ca and N$_{t}$ in soils. Whereas Chodak and Niklińska [19], reported that tree species had a significant impact on the chemical and microbial properties of mine soils mainly by increasing soil pH, C and Nt content.

Table 8. Mean values and standard deviations for pH, EC, content 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.

		LS-c	LS-B	LS-P	HS-c	HS-B	HS-P
pH	s	1.8^{b3} ± 0.04	1.8^{b} ± 0.02	1.8^{b} ± 0.10	2.2^{b} ± 0.03	2.2 ± 0.10	2.3^{b} ± 0.1
	f	2.5^{a} ± 0.08	2.8^{a} ± 0.12	3.8^{a} ± 0.26	2.6^{a} ± 0.18	2.2 ± 0.22	2.9^{a} ± 0.2
				mS cm^{-1}			
EC	s	10.80 ± 1.38	11.48^{a} ± 0.42	10.91 ± 3.07	4.85^{a} ± 0.29	5.52 ± 0.77	4.51^{a} ± 0.4

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	f	1.12^{b} ± 0.32	0.71^{b} ± 0.23	0.10^{b} ± 0.03	2.74^{b} ± 0.34	4.75 ± 1.00	2.40^{b} ± 0.3
		mg l^{-1}					
St	s	1570. ± 156.5	1585. ± 100.1	1583. ± 428.6	814.3^{a} ± 31.4	841.4 ± 73.6	741.0^{a} ± 74.
	f	71.0^{b} ± 20.3	53.7^{b} ± 17.2	9.6^{b} ± 4.6	625.7^{b} ± 36.6	725.4 ± 63.6	588.0^{b} ± 24.
DOC	s	82.84 ± 8.95	92.97^{a} ± 9.38	117.1 ± 18.80	101.41^{a} ± 9.54	127.0 ± 33.11	110.37^{a} ± 15.
	f	5.08^{b} ± 0.33	20.47 ± 3.17	37.20 ± 10.72	9.78^{b} ± 1.65	32.00 ± 4.03	29.56^{b} ± 2.4
Nt	s	14.65 ± 1.97	18.05^{a} ± 1.02	16.42 ± 4.11	5.72^{a} ± 0.31	7.68^{a} ± 1.55	6.54^{a} ± 0.6
	f	0.53^{b} ± 0.04	1.46^{b} ± 0.17	1.17^{b} ± 0.33	0.43^{b} ± 0.02	2.58^{b} ± 0.67	0.82^{b} ± 0.0
C	s	474.4 ± 39.07	445.3 ± 26.10	442.7 ± 33.14	550.23^{a} ± 17.79	552.7 ± 14.18	553.38 ± 50.
	f	5.84^{b} ± 1.28	13.66 ± 4.08	5.20^{b} ± 6.11	467.27 ± 24.03	494.7 ± 21.99	495.56 ± 17.
Mg	s	2.21^{a} ± 1.73	7.85^{a} ± 1.48	8.01^{a} ± 3.14	0.01^{c} ± 0.00	1.62^{ad} ± 0.96	0.85^{d} ± 1.7
	f	0.01^{b} ± 0.00	0.68^{b} ± 0.12	0.07^{b} ± 0.14	0.01^{c} ± 0.03	2.24^{a} ± 0.49	0.48^{d} ± 0.0
Al	s	73.24 ± 12.42	61.17^{a} ± 6.95	60.68 ± 25.23	42.95^{a} ± 6.32	32.42 ± 10.98	21.66^{a} ± 9.2
	f	0.22^{b} ± 0.16	0.05^{b} ± 0.04	0.06^{b} ± 0.04	0.74^{b} ± 0.41	1.77^{b} ± 0.47	0.21^{b} ± 0.1

[1]s –at the beginning of experiment; [2]f – after 12 weeks; [3]different letters indicate significant differences in the measured values

The obtained results of the experiment indicated that an addition of litter, especially in the case of the most sulfur-contaminated soil, is not sufficient for detoxification in the short period (12 weeks). Probably in hot spots where previous neutralization was ineffective or not thorough, it will have to be repeated with higher doses of the neutralizer in the form of sludge lime, as it was done on most of the former Jeziórko mine [4]. Subsequently, in the next stage, it will be possible reforestation, which will gradually provide litterfall and organic matter which plays a key role in soil-forming processes. Judging from the experiences describing a similar study with post-mining substrates [17] but from other types of facilities (not as sulfated), 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 highly sulfated soils without neutralization, this will be a very long process.

4. Summary and conclusions

Based on comprehensive research, it was found that on reclaimed and afforested areas of the Jeziórko mine, there are still hot spots highly contaminated with sulfur. They cover a relatively small area of about 2% of the monitored site (216.5 ha). However, they typically display a significant disturbance of soil and surface water chemistry, affecting the reaction of vegetation. The investigated surface waters mostly display relatively high pH (6.5 on average), and only in several points (3 out 15) did pH range from 2.6 to 3.1 indicating heavy acidification and AMD risk. These surface water properties were also accompanied by an elevated concentration of sulfate ions SO_4^{2-} (mean of 935.13 mg L^{-1}) and high EC (mean of 1,795 µS cm^{-1}) with a simultaneous high concentration of Ca^{2+} ions (from 175 to 434 mg L^{-1}), which was related to the neutralization of sulfurous soils with the use of sludge lime. It was found that at sulfur concentration in soils of up to 3% after suitable neutralization with sludge lime (at a minimum dose of 500 Mg kg^{-1}) the introduced birch and pine stands displayed good growth parameters and viability. The remaining ones, occurring in spots, constituting about 2% of heavily contaminated sites, where neutralization was not done properly, provide opportunities for studying sulfur biogeochemistry and monitoring long-term changes in the reconstructed forest ecosystem, especially reactions of vegetation to environmental stress.

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Wood small-reed proved extremely resistant to sulfur contamination and relatively high salinity of soils occurring even on extremely sulfated soils. There is therefore a perspective and an indication of the use of this species in natural succession of similar sites as alternative temporary biological stabilization.

Significant reduction of sulfur concentration in composites as a result of rinsing will take place in contaminated environment for a long time and soil detoxification will not be achieved without neutralization. Changes in the chemistry of the soil solution after the addition of organic matter were due to the process of litter mineralization and leaching of nutrients. This effect was more pronounced in the case of birch litter addition when increased nitrogen and magnesium leaching occurred, which is important in the perspective of soil-forming processes and plant nutrition..

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