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Original Research

Chemical Degradation of Forest Soil as a Result of Polymetallic Ore Mining Activities

Milan Bussinow[1], Borivoj Sarapatka[1]*, Pavel Dlapa[2]**

[1]Department of Ecology and Environmental Sciences, Faculty of Science, Palacky
University, tr. Svobody 26, 771 46 Olomouc, Czech Republic
[2]Department of Soil Science, Faculty of Natural Sciences, Comenius University,
Mlynska dolina B-2, 842 15 Bratislava, Slovak Republic

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Abstract

The results of research conducted in the surroundings of a former polymetallic mine near the town of Zlaté Hory, North Moravia, Czech Republic, are presented. A by-product of the ore flotation technique was 6.8 million tons of metalliferous tailings. The adjacent forest area is contaminated by wind-blown pyritic dust particles. The experimental profile was located in a spruce monoculture down wind of the tailings. Samples of soil were taken at 50 m intervals. Ten soil pits were dug and soil samples were taken from the artificial top layer of deposited tailing dust, as well as from the Ah and Bw horizons. Soil samples were analyzed using AAS in order to obtain total heavy metal content of Cu, Zn, Pb, Cd and soluble forms of Al and Fe. The content of accessible nutrients (Mg, Ca, and K) was measured, as well as the content of organic carbon and the ratio of phosphorus retention. Both active and exchangeable soil pH was measured. Our results showed that the main problem is not heavy metal contamination per se, but rather severe acidification. The oxidation of pyrite has resulted in a decrease in pH (pH/H_2O ranging from 3.1 to 4.1). The final values for Al and Fe solubility fall within either the aluminium or iron buffer ranges. Such severe acidification has led to increased toxic Al mobilization, the serious leaching of mineral nutrients (Mg: <0.05-34 $mg\cdot kg^{-1}$, Ca: 0.6-244 $mg\cdot kg^{-1}$, and K: <0.1-108 $mg\cdot kg^{-1}$), and a high degree of irreversible retention of phosphorus (90-95%).

Keywords: tailings, pyrite, soil degradation, acidification, heavy metals, nutrient availability

Introduction

Mining activities are often connected with various environmental problems. The extent of any potential burden depends on the mining and processing techniques used and on the nature of the mined material. Oxidation of metal sulphides in mines, mine dumps and tailings produces acidic metal-rich water that can acidify and contaminate surface water, groundwater, sediment, and soil. These processes have been recognized as an important environmental problem over the past decades and various aspects of mining impacts have been investigated [1-4].

Mine tailings contain various gangue minerals (silicates, carbonates, oxides, and metal sulphides) that have been separated from the ore concentrate [5]. Tailings are typically ground into fine sand to silt-size particles and thus have increased reactivity compared to original ore material. Exposure of tailing sulphides to the atmosphere and water typically results in the oxidation of ore-associated sulphides accompanied by the formation of acid mine drainage [6]. It is precisely the oxidation of sulphide minerals which is the primary process that causes problems [7].

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*e-mail: borivoj.sarapatka@upol.cz
**e-mail: pavel.dlapa@fns.uniba.sk

Oxidation of iron sulphide minerals (pyrite of pyrrhotite) generally are dominant in mining waste materials [7]. Many studies have been conducted on pyrite oxidation, and two reviews have been presented by Nordstrom and Southam [8] and Nordstrom and Alpers [9].

Oxidation of other sulphide minerals, e.g. sphalerite, chalcopyrite, galena, and arsenopyrite, is responsible for the release of heavy metals as stated by Malmstrom et al. [7]. Jambor [10] reported a general sequence of oxidizing tendencies for the important sulphide minerals in tailings, going from readily attacked to increasingly resistant: pyrrhotite > galena-sphalerite > pyrite-arsenopyrite > chalcopyrite. In laboratory experiments Gleisner and Herbert [11] found that metal release from pyrite-rich tailings decreased in the order Cu > Zn > Fe, which implied that pyrite was more resistant to weathering than sphalerite and chalcopyrite. However, under natural conditions the release of trace elements from mining waste materials results from complex biological, geochemical, and physical processes [2].

In tailing material, processes that buffer pH by consuming protons are important, since these processes may thus reduce acid drainage. Calcite is the most effective acid neutralizing mineral because it consumes protons faster than the rate at which pyrite oxidation proceeds. Among silicate minerals the weathering rates for plagioclase and K-feldspars are much slower than pyrite oxidation, and Mg-chlorite weathering [12] is even slower. Field studies have shown that Mg and Al can be depleted in the weathered zone of tailing deposits due to chlorite dissolution where about 50-75% of the acidity produced from sulphide oxidation was neutralized by Mg-chlorite dissolution [13].

In soils potentially affected by products of tailing weathering many chemical characteristics, the availability of plant nutrients (Ca, Mg, P, etc.), microbial activity [14], the presence and mobility of toxic concentrations of certain ions (Al, Mn, heavy metals), and different physicochemical characteristics are pH-controlled. In the tailing leachates a high concentration of different ions occurs, which causes precipitation of secondary minerals, especially when pH is increasing. Commonly reported secondary minerals include iron oxides (ferrihydrite, lepidocrocite, and goethite), gypsum, jarosite, schwertmannite, and anglesite [11].

The present article focuses on a detailed characterization of the impact of mine tailing deposition onto soils under spruce forests. The aim was to identify chemical degradation processes and to relate the impact-to-soil characteristics, and ultimately to assess the extent of soil degradation on a particular site.

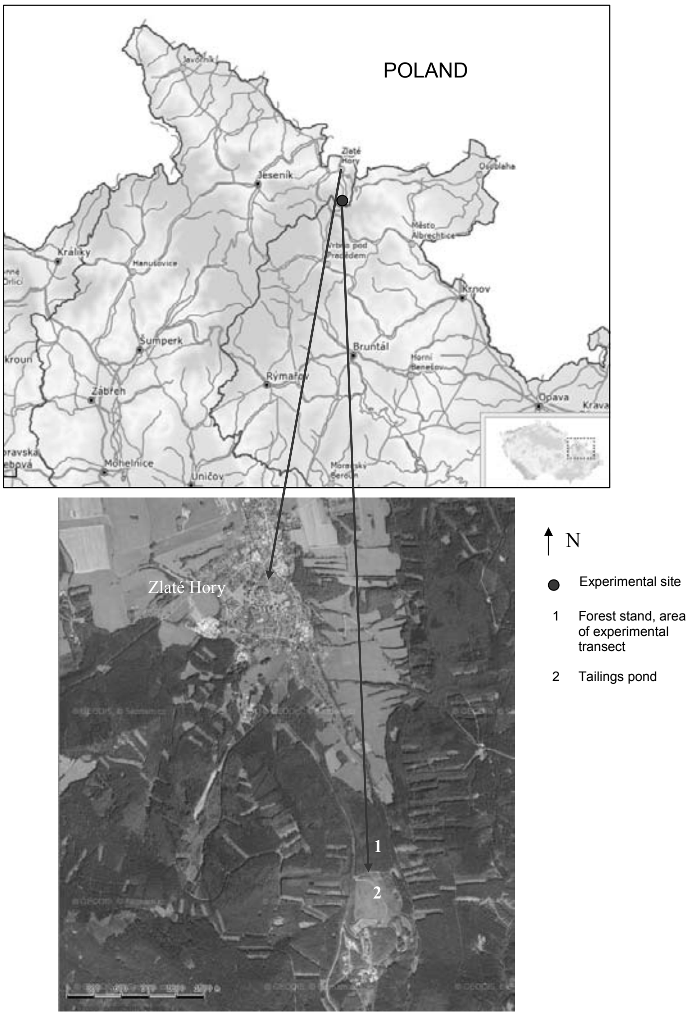


Fig. 1. The location of the experimental site.

Experimental Procedures

Investigation Area

The experimental field is located in Moravia, in the eastern part of the Czech Republic, near the town of Zlaté Hory. Mining of various ores dates back to the Middle Ages, with the modern era of intense mining activity undertaken in the 1950s, when an ore processing factory was built 5 km south of Zlaté Hory (Fig. 1).

A flotation technique was used to obtain polymetallic concentrates. Sulphide ores generally contain a large proportion of worthless gangue minerals, meaning that the ores need to be processed to extract the metals. Flotation is a complex process in which valuable minerals are separated from gangue minerals. The separation is based on the surface properties of each mineral phase present in the suspension. It is necessary to grind the material to very fine particle size in order to improve mineral liberation [15, 16]. The mine tailings normally contain a variety of residual sulphides (e.g. pyrite FeS_2), heavy metal particles, and various chemicals used during the flotation process. Active mining and ore processing in the area ended in 1993 due to low profitability. During the last four decades of ore processing in the area under study, about 6.8 million tons of metalliferous tailings were stored in a tailings pond constructed adjacent to the mill. The pond is located in a narrow mountain valley open to prevailing winds from the south and southwest, and blowing toward the town of Zlaté Hory. Wind, in this case, is one of the major vectors of pollution. Wind-borne particles have accumulated in a neighboring Norway spruce monoculture. Here, the oxidation of sulphide minerals connected with the various ore-processing chemicals has strongly affected soil and vegetation.

Since active mining came to an end in the late 1980s and the tailings pond was then remediated, we summarize only published data on the material from the tailings pond. Mine tailings deposited in the pond contain on average: 69.7% SiO_2, 0.38% TiO_2, 7.4% Al_2O_3, 10.6% Fe_2O_3, 0.10% MnO, 1.5% MgO, 1.0% CaO, 0.55% Na_2O, 1.2% K_2O, 0.60% C, and 4.6% S [based on data from 18]. Petrology of the tailing material is characterized by the predominance of quartzite, mica schist and pyrite, with low content of heavy metals [17]. Total contents of selected heavy metals in the tailings (deposited in the pond) obtained from 35 drill hole samples are given in Table 1 [18].

Experimental Transect

In order to find general trends in both the vertical and horizontal distribution of chemical properties, we designed an experimental transect and set it in the studied area. The transect ran from below the tailings pond (the first soil probe was dug at the edge of the directly adjacent spruce monoculture) and continued into the forest following the prevailing wind direction. Soil pits were dug at 50 m intervals; a total of 10 soil profiles were sampled. The burden resulting from windblown tailing dust was especially obvious within the first 15 m from the forest edge, where a large proportion of spruce had either been seriously damaged or killed; almost no herbal undergrowth had developed (except for vigorous associations of pioneer moss species) and there was a noticeable odour of sulphuric reaction products.

Table 1. Total contents of Cd, Cu, Pb, and Zn ($mg \cdot kg^{-1}$) in tailings deposited in the pond obtained from 35 drill hole samples [18].

	Tailings in the pond			
	Min	Max	Mean SD	Median
Cd	0.1	16.8	1.5 3.4	0.5
Cu	54	6371	883 1,128	505
Pb	17	855	88 144	51
Zn	60	2280	326 452	157

Soil Sampling

Haplic Cambisol Dystric (WRB, 2006) is the most common soil type in this area. Samples from three layers were collected: the deposited metalliferous dust, the original Ah, and the Bw horizons. Approximately 2.5 kg of soil samples and metalliferous dust were stored in marked plastic bags. The samples were then prepared for analysis: air-dried at room temperature and ground to pass through a 2 mm plastic sieve.

To obtain data on the total amount of deposited metalliferous dust along the experimental profile, we collected the dust material from five 100 cm^2 areas at each soil probe. The dust was then air-dried and weighed. The amount obtained was then expressed per 1 m^2. (See Figs. 2 and 3 for photographs of the experimental area and a typical soil profile).

Laboratory Methods

Soil pH values (H_2O, 0.01M $CaCl_2$) were determined after 24-hour equilibration at a soil:solution ratio of 1:5. Total organic carbon was measured with oxidation with $K_2Cr_2O_7$-H_2SO_4 and titration of non-reduced chromate. Amounts of accessible nutrients Ca, Mg, and K were determined with AAS in Mehlich II extracts containing 0.2M CH_3COOH, 0.015M NH_4F, 0.2M NH_4Cl, and 0.02M HCl [19, 20].

To measure solubility of Al and Fe, the soil samples were equilibrated for 24 hours with 0.01M $CaCl_2$ (soil: solution ratio of 1:5), filtered through a 0.1 μm membrane filter and then analyzed with AAS.

Phosphorus retention was determined according to the Soil Survey Laboratory Methods Manual [21]. A 5g soil sample was shaken with 1,000 ppm P solution (containing KH_2PO_4, $CH_3COONa{\cdot}3H_2O$, CH_3COOH) for 24 h. The mixture was filtered and an aliquot of the filtrate was transferred to a colorimetric tube to which nitric vanadomolybdate acid reagent (solution containing NH_4VO_3 and HNO_3) was added. The percentage transmittance of the solution was read using a spectrophotometer.

To obtain total heavy metal content (Pb, Cd, Cu, Zn) the soil samples were mineralized in a microwave digestion unit (BM-1S/II). Each sample (0.200 g) was placed in a Teflon vessel with HNO_3 (3 ml), HCl (2 ml) and H_2SO_4 (1 ml) and then digested. The solution was thereafter filled to 50 ml volume with distilled water and analyzed using AAS.

Analysis for Al, Cd, Cu, Fe, Pb, Zn, Mg, Ca, and K was performed with flame atomic absorption using 1GBC AAS Avanta Σ. The detection limits of Al, Cd, Cu, Fe, Pb, Zn, K, Mg, and Ca were 0.028, 0.013, 0.001, 0.02, 0.06, 0.005, 0.1, 0.05, and 0.05 mg·kg^{-1}, respectively.

Fig. 2. A general view of the experimental area: remediated tailings pond (right) and adjacent forest stand where the experimental sampling profile was situated.

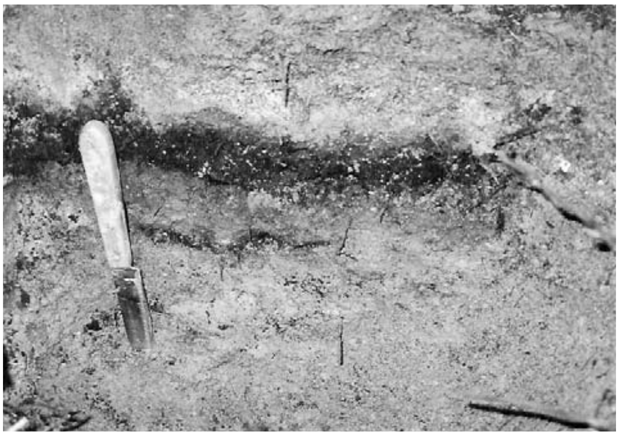


Fig. 3. Typical soil profile along the experimental transect with a surface greyish layer of wind-deposited tailings, dark Ah horizon, and bottom brown-orange Bw horizon.

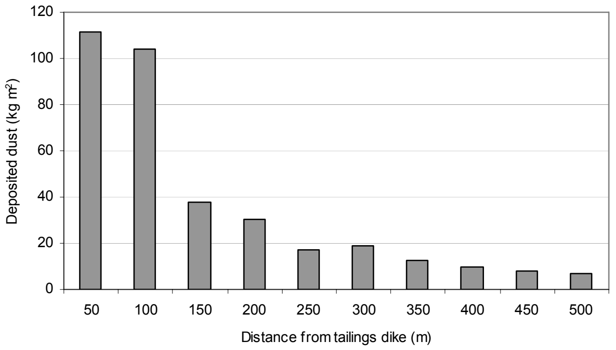


Fig. 4. Total amount of wind-deposited tailings (pyrite-containing dust) along the transect. The layer of deposited tailings was separated from the buried Ah horizon, dried, and weighed. The graph shows a steep decrease 100 m from the dike; from sampling site No. 3 the decrease is balanced toward the end of the transect. However, despite this decrease the concentration of some elements per unit weight of analyzed tailings increases with distance.

Results and Discussion

Soil processes are, to a large extent, influenced by a considerable amount of wind-deposited material (Fig. 4). In the case of the first two sampling sites this amount even exceeded 100 kg of flotation dust per square meter. At soil pit No. 3 the total amount of deposited tailings steeply drops below 40 kg/m^2 and then decreases more or less continuously along the experimental transect. We can conclude that the pollution load decreases with distance as in a study conducted in Poland [22], where the concentration of measured metals tends to increase with greater proximity to the pollution source.

Soil pH is one of the soil characteristics that plays a crucial role because pH influences other soil processes, e.g. those connected with nutrient availability and the mobility of potentially toxic elements such as heavy metals. Fig. 5 shows pH values (H_2O, $CaCl_2$) for three soil horizons in individual soil profiles as well as the general pH gradient along the transect. The results reveal serious acidification of the soils, even reaching the mineral Bw horizon. In the top layer, which contains deposited tailings, the pH/H_2O falls within a quite narrow range, between 3.4 and 3.5 (pH/$CaCl_2$ 3.0-3.3); the Ah horizon is even more acidic, with values from 3.2 to 3.5 (pH/$CaCl_2$ 2.9-3.0). In the case of the Bw horizon, pH values vary from 3.1 (pH/$CaCl_2$ 2.8) at the beginning of the transect to 4.1 (pH/$CaCl_2$ 3.9) at the end, with a sharp increase discernible from the middle of the transect (sampling sites 4 and 5). The extremely low pH values give evidence of a shift in the analyzed soil horizons to the aluminium or even iron buffer ranges [23] due to the increasing acid load.

For clarity of presentation, the statistical analysis of the aforementioned data refers to several different phenomena from which the character of chemical degradation at this particular site may be viewed. General statistical data summarizing the results obtained from all sampling

Table 2. Summarized statistics (minimum, maximum, mean, standard deviation, and median) of measured soil properties. Content of organic carbon as % and other elements in mg·kg^{-1}.

	Tailings				Ah horizon				Bw horizon			
	Min	Max	Mean SD	Median	Min	Max	Mean SD	Median	Min	Max	Mean SD	Median
pH/H_2O	3.4	3.5	3.5 0.04	3.5	3.2	3.5	3.4 0.1	3.4	3.1	4.1	3.6 0.4	3.6
pH/$CaCl_2$	3.0	3.3	3.2 0.1	3.2	2.9	3.0	3.0 0.1	3.0	2.8	3.9	3.3 0.4	3.3
C_{org}	0.08	4.7	1.9 1.6	1.6	15	21	18 2.0	17	0.09	2.0	0.8 0.6	0.9
Al_s	128	768	336 208	235	75	1194	469 379	315	341	1940	1263 583	1407
Fe_s	260	9961	4731 3160	4003	8274	13651	11031 1854	10804	48	4425	1117 1466	708
K	NM	45	20 18	17	24	108	53 28	42	NM	26	13 7.9	14
Ca	6.1	81	34 25	29	81	244	121 50	103	0.6	55	27 15	26
Mg	NM	6.5	1.6 2.6	NM	6.0	34	13 8.1	11	NM	5.5	2.5 2.0	3.0
Cd	NM	1.5	0.6 0.6	0.5	NM	2.7	0.9 0.8	0.9	NM	2.0	1.0 0.7	0.9
Cu	48	101	74 17	69	53	140	92 27	86	48	127	76 26	71
Pb	56	94	69 11	66	33	99	55 21	52	40	73	56 11	58
Zn	41	71	56 8.8	56	16	53	29 9.6	27	33	54	44 7.2	45

Mean – arithmetical mean; SD – standard deviation; NM – not measurable; pH/H_2O, pH/$CaCl_2$ – soil pH measured in water and 0.01M $CaCl_2$, respectively; C_{org} – organic carbon content as %; Al_s, Fe_s – 0.01M $CaCl_2$ soluble content of aluminium and iron in mg·kg^{-1}; Pb, Zn, Cu, Cd – total content of heavy metals in soils in mg·kg^{-1}; K, Mg, Ca – Mehlich II extractable content of nutrients in mg·kg^{-1}

sites is given in Table 2. More detailed information on the content of both the metal and nutrient elements in individual soil profiles, as well as trends in their horizontal distribution along the experimental transect, are given in Figs. 6 and 7. All results are reviewed and discussed below.

Aluminium and iron solubility, measured in the equilibrium extracts of 0.01 M $CaCl_2$, showed that acidification resulting from pyrite oxidation seems to be the main degrading process. The net reaction of complete oxidation of pyrite, hydrolysis of Fe^{3+} and precipitation of iron hydroxide produces 4 H^+ per mol of pyrite. Thus pyrite oxidation is the most efficient producer of acid of the common sulphide minerals [24]. Released acidity causes a fall in soil pH and an increase in both Al and Fe solubility to toxic levels (Fig. 8).

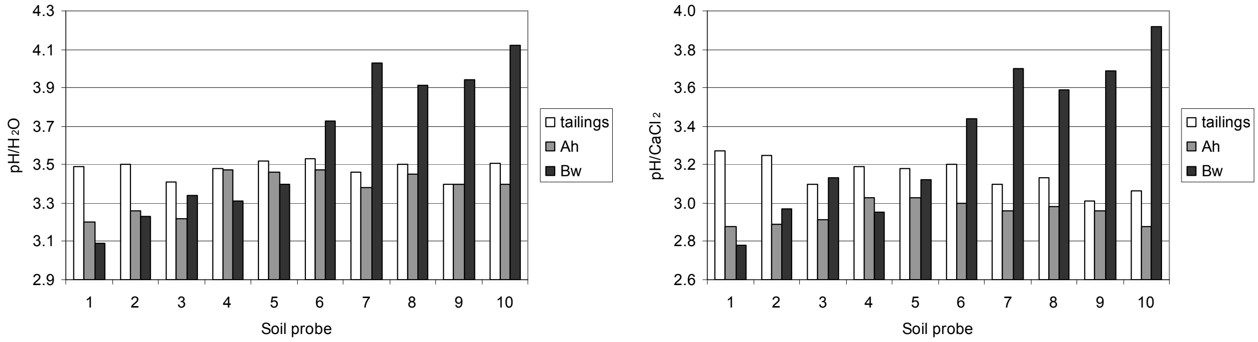


Fig. 5. Soil pH values (measured in H_2O or 0.01M $CaCl_2$) of analyzed soil horizons (layer of wind-deposited tailings, Ah, and Bw soil horizons). The oxidation of pyrite contained in the tailings has resulted in a decrease in pH/H_2O from an initial value of 4.5-5.5 to current values, which range from 3.1-4.1. Thus, the soil horizons fall within either the aluminium or even the iron buffering range.

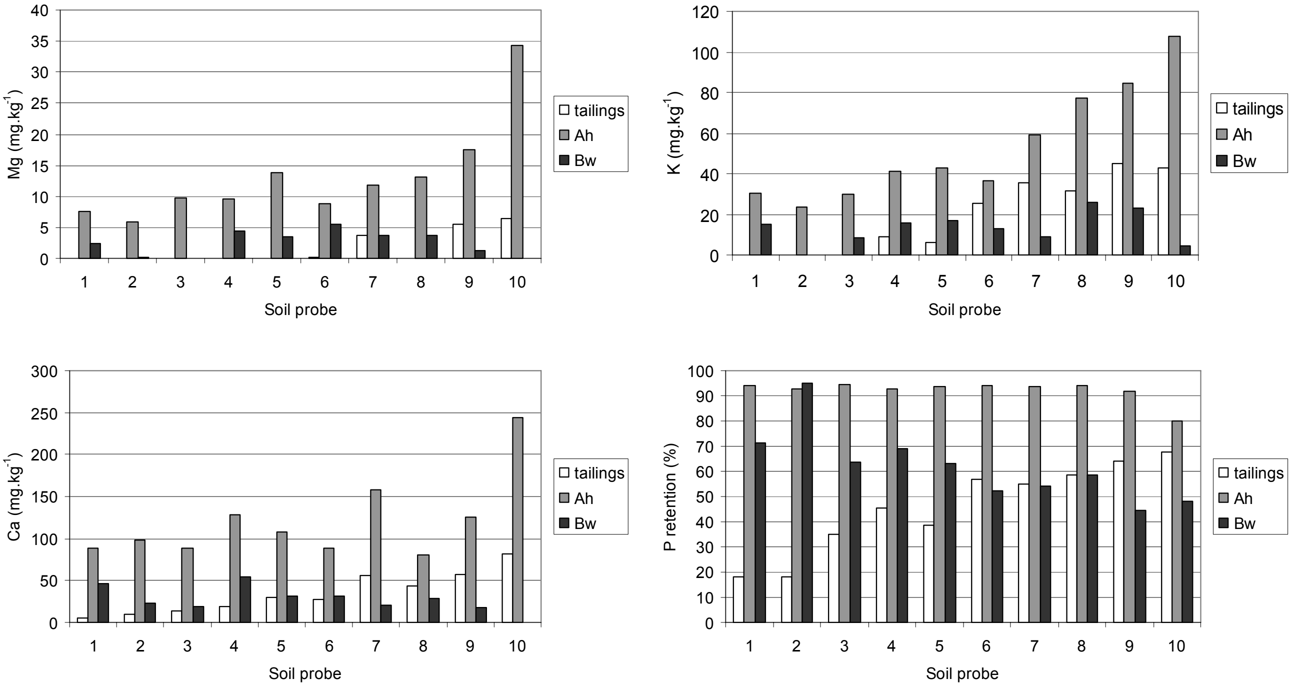


Fig. 6. Content of accessible nutrients (Mg, Ca, and K) and phosphorus retention along the experimental transect.

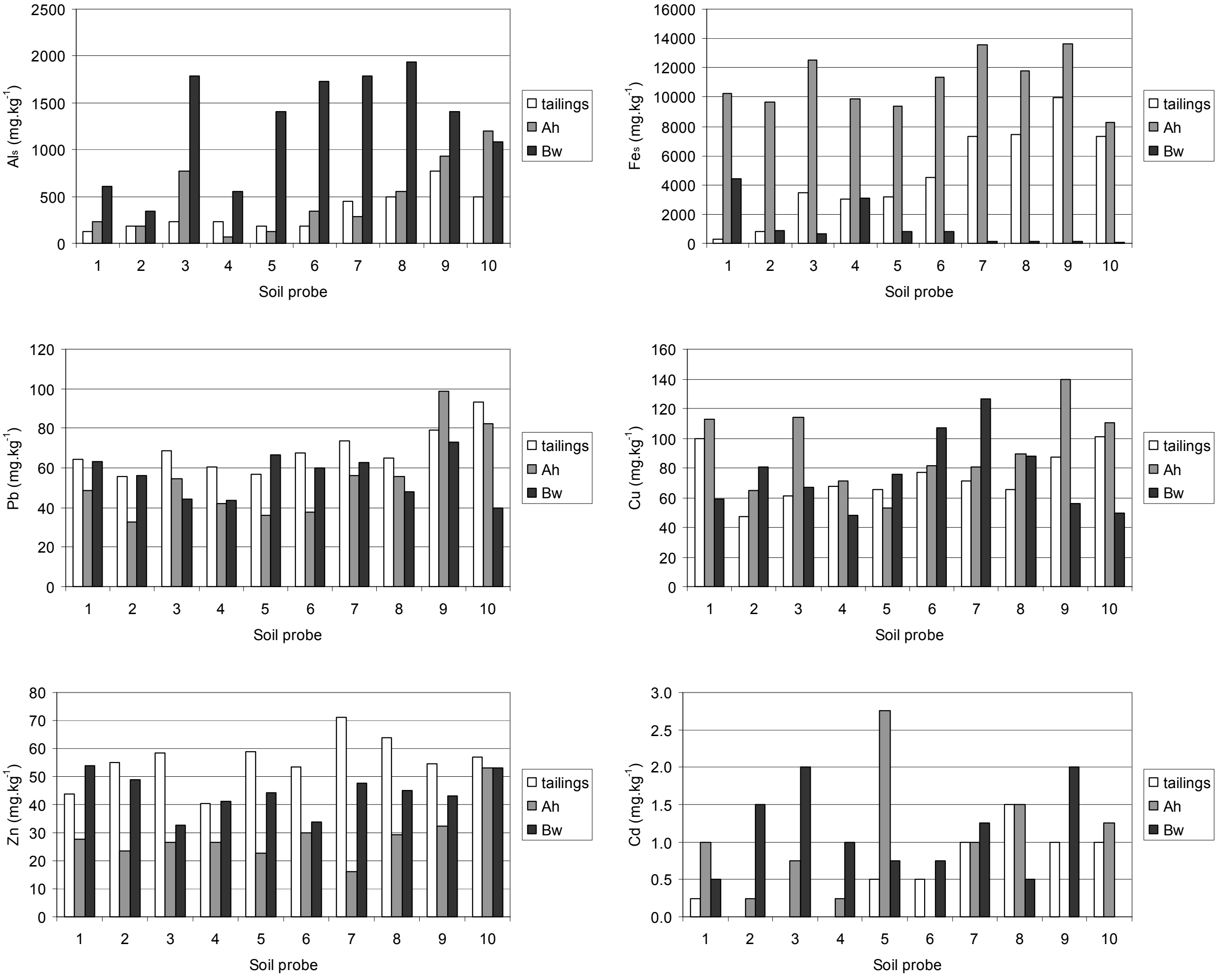


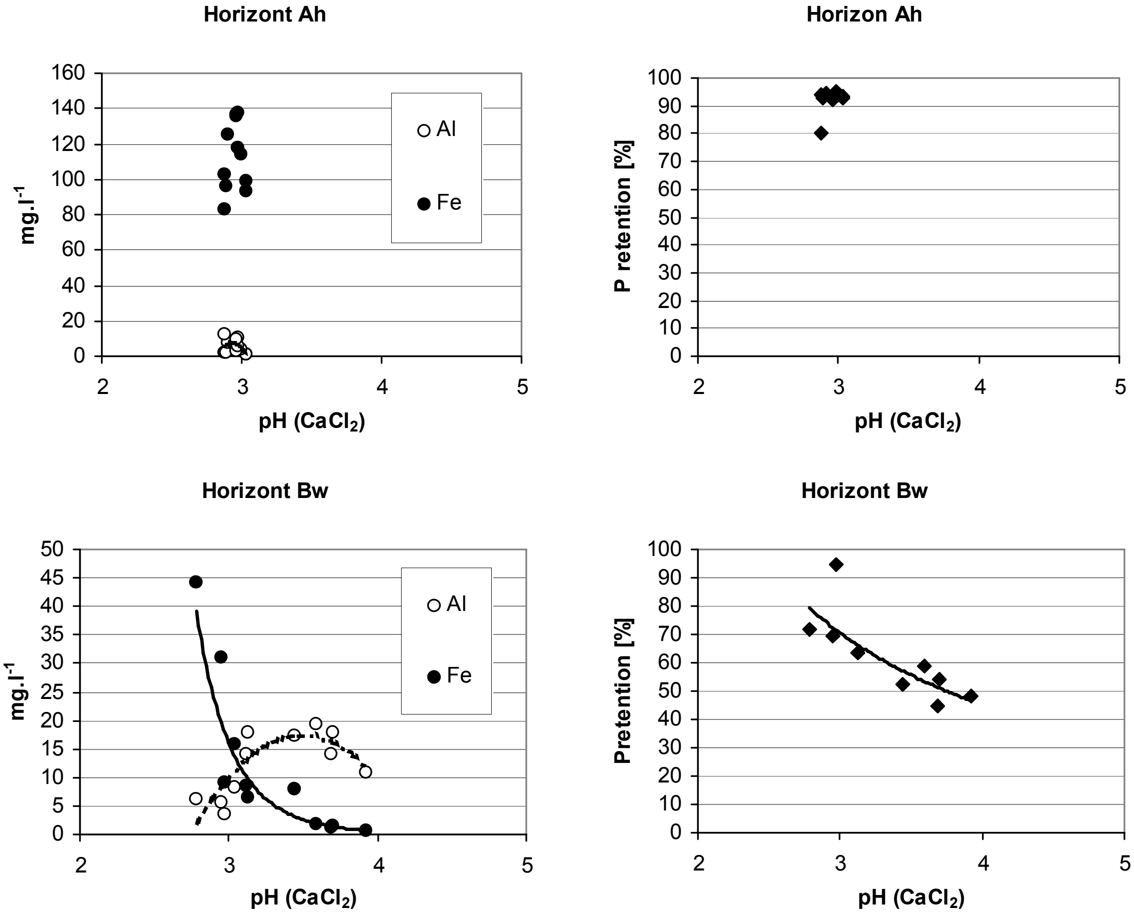
Fig. 7. Metal content in soils along the experimental transect.

As can be seen in Fig. 8, acidification inside the Ah horizon reached the iron buffer range [23] – pH values close to 3. Under such conditions soil acidity is maintained by precipitation and dissolution processes of iron hydroxides. The Ah horizon is enriched with iron hydroxides precipitated from tailing solutions. Various iron mineral phases may precipitate from pyrite oxidation products, such as ferrihydrite, schwertmannite, goethite or jarosite, depending on pH-Eh conditions and availability of potassium and sulphur [24]. There is no significant trend along the transect as acidification in the Ah horizon of all soil profiles stops in the iron buffer range.

A different situation occurs in the Bw horizon (Fig. 8). In soils degraded to a lesser extent we are still able to observe the Al buffer range with hydrated Al oxide dissolution as the main proton-neutralizing process. As the degradation intensifies toward the tailings pond, even the Fe buffer range can be found in the Bw horizon. This situation is characterized by an exponential increase in Fe solubility and the parallel leaching of Al, as can be seen in the lower part of Fig. 8. Soil acidity drops to a pH value approaching 3 in the most degraded Bw horizon. The decrease in Al solubility toward the tailings pond can also be attributed to iron coatings on soil particles, precipitated from tailing leachates due to gradual increase of pH with soil depth, resulting in inhibited phyllosilicate weathering [25].

In general, we can conclude that while acidification caused by the influence of acid rain usually remains in the Al buffering range with pH around 4, on our experimental site the pyrite weathering products caused such an extreme acid load that the acidification remains in the Fe buffer range characterized by pH values close to 3. Such severe acidification results in an increase in aluminium toxicity and a decrease in nutrient availability. This alteration in soil conditions can seriously affect soil biota and especially the vegetation cover. Increased concentrations of iron can attack the tissues in organisms by peroxidation of lipids. This causes the release of hydroxyl free radicals, which can attack proteins, especially those in intestines, and finally cause death [26]. Moreover, Al adversely affects plant development through antagonistic interference in the uptake of particular cations, such as Ca^{2+} and Mg^{2+} [27]. Acidification would reduce exchangeable base cations and increase the content of aluminium [28]. The Ca+Mg+K to Al ratio is now the most common chemical criteria for assessment of acid critical load in forests [29].

Fig. 8 also describes the influence of decreasing pH on phosphorus retention in soil. We consider P retention exceeding 85% as extreme. As can be seen in the Ah horizon, P retention exceeds 90% in all soil profiles. In the case of the Bw horizon we observe an increase in P retention in close relationship with increasing soil degradation, and we can also see how P retention is connected with increasing Fe solubility. Various mechanisms behind the retention of phosphorus, including precipitation and specific sorption, are enhanced by the decrease in soil pH and increase in Al


Horizont Ah

Horizon Ah

Horizont Bw

Horizont Bw

Fig. 8. Aluminium and iron solubility and phosphorus retention in Ah and Bw horizons of affected forest soils.

or Fe content in soils [30, 31]. Fig. 8 shows that P retention follows a different pattern in each soil horizon. The observed degree of P retention results in a lack of accessible phosphorus for vegetation.

The aforementioned findings are in agreement with those of Golez and Kyuma [32] who studied the influence of pyrite oxidation and soil acidification on some essential nutrient elements.

Correlation analysis (Table 3) of available data indicates statistically significant relationships, particularly in the dependence of individual chemical parameters on the distance from the source of pollution. Significant correlation was found most frequently in the tailings layer. The distinct changes along the transect are evidenced by correlation coefficients between distance and Corg, pH/$CaCl_2$, soluble content of Al and Fe, major (Mg, Ca, K) and trace (Pb, Cd) element content (Table 3). Close relationships between chemical properties and element contents can be considered a result of wind erosion-transport-accumulation processes with coarse and heavy particles accumulating close to the tailings pond and an increase in fine and light fractions with increasing distance along the transect. In addition, chemical processes taking place in the tailings layer, especially acidification and leaching, caused further changes in chemical properties and composition of tailing material deposited on the forest soil surface.

Miller et al. [33] studied metal leaching under acidic conditions in soils containing sulphide minerals. They reported significant leaching of metals depending on soil type. Dijkstra et al. [34] characterized the leaching process of heavy metals (including Pb, Cd, Zn, and Cu) in contaminated soils for a very wide pH range (pH from 0.4 to 12). They demonstrated that a concentration of heavy metals may fall over 2 orders of magnitude between pH 2 and neutral pH. Comparison of various reactive surfaces showed the importance of soil organic matter, iron and aluminium (hydr)oxides with respect to metal sorption under acidic conditions. The leaching process at low pH values is affected by weaker metal sorption to variably charged surfaces due to competition for surface sites by protons and repulsive charge effects [34].

In the metalliferous tailings layer we can even see a negative correlation between distance and pH/$CaCl_2$. Such a trend can be attributed to change in grain size distribution of tailing material deposited on the soil surface. The content of the fine-grain-sized fraction of tailing increases with distance from the tailings pond. Al and Fe ions from tailing material carry secondary acidity and cause intensive acidification [35]. In finer tailing material the content of the exchangeable fraction of Al and Fe ions is higher and consequently the exchange reactions in $CaCl_2$ suspension cause a release of a higher amount of Fe and Al ions and a decrease in tailing pH/$CaCl_2$ with increasing distance from the tailings pond.

Heavy metal content revealed a positive correlation with distance along the transect in the case of Pb and Cd, but no relationship was found for Zn and Cu. Analysis of heavy metal content in soils (Table 2) did not indicate distinct pollution with heavy metals. From the results obtained it follows that tailing material deposited on the forest soil surface did not contain harmful amounts of heavy metal sulphides, except that of pyrite. Only total content of Cu in the Ah horizon exceeds the B limit (100 $mg \cdot kg^{-1}$) from the Dutch standard, often used as reference values [36]. Otherwise there are some weak trends in heavy metal content (Fig. 7).

Correlation relationships observed in the tailings layer are partially reflected in the degraded Ah horizon. Strong acidification and element content depends directly on composition and leaching from tailings cover. The observed relationships are therefore similar, and significant correlation with distance of major and trace elements still occurs (Table 3).

In the case of nutrients present as cations (K^+, Mg^{2+}, Ca^{2+}), acidification caused them to be leached out from the soil profile (Fig. 6). This leaching is connected with high Fe^{3+} and Al^{3+} concentrations in the soil solution and the consequent displacement of the base cations bound to soil colloids. We found a positive correlation between distance and content of accessible K and Mg in the Ah horizon and the tailings layer. We especially consider the content of accessible Mg below10 $mg \cdot kg^{-1}$ to be extremely low compared to published deficiency limits [e.g. 37].

In the Bw horizon, however, soil acidification just begins to be a major degrading process with the strongest correlation between soil pH and distance from the tailings pond. Consequentially, iron solubility also correlates with distance at 0.05 and 0.01 significance level, respectively. But no significant correlation was observed for other soil properties and element content (Table 3).

Although the area under study is to some extent contaminated by potentially toxic elements, severe acidification seems to be the major process influencing conditions in the soil environment.

Conclusions

Analysis of deposited tailings and of underlying soil horizons revealed strong chemical degradation caused by oxidation of pyrite particles contained in the tailings. Correlation analysis of available data indicates close relationships, particularly in the dependence of individual chemical parameters on the distance from the source of pollution. It seems that the main effect of these tailings is soil acidification. Soil pH fell to values close to 3 and, as such, the analyzed soil samples can be characterized by either the iron or aluminium buffer range. Under such conditions most base cations such as Ca, Mg, and K are leached out and the irreversible retention of phosphorus in most cases exceeds 90%. In the tailings layer and Ah horizon heavy metal content revealed positive correlation with distance along the transect in the case of Pb and Cd, but no relationship was found for Zn and Cu. However, the results obtained do not indicate distinct pollution by heavy metals. The anthropogenic soil degradation and altered ecological conditions have a visible impact on contiguous vegetation.

Table 3. Correlation matrix for (a) Tailings, (b) Ah horizon and (c) Bw horizon.

(a) Tailings	Distance	pH/H_2O	pH/$CaCl_2$	C_{org}	Al_s	Fe_s	Pb	Zn	Cu	Cd	K	Mg	Ca
Distance	1.00												
pH/H_2O	-0.05	1.00											
pH/$CaCl_2$	-0.81**	0.59	1.00										
C_{org}	0.93**	-0.13	-0.80**	1.00									
Al_s	0.83**	-0.49	-0.87**	0.86**	1.00								
Fe_s	0.94**	-0.35	-0.90**	0.88**	0.93**	1.00							
Pb	0.74*	-0.24	-0.75*	0.72*	0.67*	0.69*	1.00						
Zn	0.47	-0.09	-0.47	0.33	0.39	0.52	0.23	1.00					
Cu	0.36	0.01	-0.25	0.41	0.31	0.28	0.69*	-0.26	1.00				
Cd	0.84**	0.04	-0.59	0.82**	0.76*	0.83**	0.52	0.61	0.33	1.00			
K	0.95**	-0.12	-0.76*	0.86**	0.87**	0.94**	0.77**	0.43	0.45	0.85**	1.00		
Mg	0.76*	-0.30	-0.78**	0.70*	0.79**	0.74*	0.90**	0.28	0.58	0.54	0.81**	1.00	
Ca	0.95**	-0.05	-0.79**	0.86**	0.79**	0.86**	0.84**	0.49	0.47	0.79**	0.92**	0.88**	1.00
(b) Ah	Distance	pH/H_2O	pH/$CaCl_2$	C_{org}	Al_s	Fe_s	Pb	Zn	Cu	Cd	K	Mg	Ca
Distance	1.00												
pH/H_2O	0.64*	1.00											
pH/$CaCl_2$	0.19	0.81	1.00										
C_{org}	0.79**	0.32	0.04	1.00									
Al_s	0.66*	-0.04	-0.44	0.47	1.00								
Fe_s	0.20	-0.05	0.14	0.50	0.13	1.00							
Pb	0.71*	0.05	-0.27	0.58	0.85**	0.34	1.00						
Zn	0.53	0.13	-0.37	0.07	0.77*	-0.44	0.57	1.00					
Cu	0.30	-0.35	-0.49	0.21	0.76*	0.41	0.83**	0.47	1.00				
Cd	0.08	0.15	0.17	0.20	-0.09	-0.33	-0.17	-0.04	-0.35	1.00			
K	0.92**	0.43	-0.07	0.71	0.76*	0.03	0.82**	0.69*	0.45	0.14	1.00		
Mg	0.77*	0.29	-0.22	0.46	0.78**	-0.29	0.70*	0.84**	0.37	0.25	0.88**	1.00	
Ca	0.60	0.21	-0.25	0.38	0.54	-0.30	0.54	0.64*	0.18	0.09	0.71*	0.86**	1.00
(c) Bw	Distance	pH/H_2O	pH/$CaCl_2$	C_{org}	Al_s	Fe_s	Pb	Zn	Cu	Cd	K	Mg	Ca
Distance	1.00												
pH/H_2O	0.96**	1.00											
pH/$CaCl_2$	0.95**	0.99**	1.00										
C_{org}	-0.49	-0.44	-0.50	1.00									
Al_s	0.52	0.59	0.59	0.12	1.00								
Fe_s	-0.70*	-0.73*	-0.77**	0.62	-0.64*	1.00							
Pb	-0.04	-0.03	-0.05	0.20	0.07	0.02	1.00						
Zn	0.07	0.08	0.07	-0.08	-0.49	0.22	0.09	1.00					
Cu	0.08	0.31	0.25	0.23	0.54	-0.39	0.30	-0.19	1.00				
Cd	-0.21	-0.18	-0.15	-0.30	0.10	-0.21	0.30	-0.49	0.05	1.00			
K	0.29	0.17	0.11	0.36	0.39	0.08	0.31	-0.17	-0.08	-0.05	1.00		
Mg	0.04	0.05	-0.06	0.59	0.26	0.21	0.23	-0.28	0.48	-0.30	0.49	1.00	
Ca	-0.60	-0.65*	-0.74*	0.68*	-0.36	0.81**	0.11	-0.12	-0.10	-0.09	0.38	0.62	1.00

Correlation is significant at the *$P<0.05$ level, **$P<0.01$ level.

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