

Evaluation of the impacts of mine drainage from a coal waste pile on the surrounding environment at Smolnica, southern Poland

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Abstract Mine drainage impacts from a coal waste pile at Smolnica, Poland have been monitored. Groundwater in an unconfined aquifer downgradient from the pile has near-neutral pH, but high concentrations of sulfate (up to 3,827 mg/l), chloride (up to 903 mg/l), and sodium (up to 2,606 mg/l). Concentrations of iron and manganese are elevated only locally, and concentrations of other metals are low. The behavior of sulfate seems to be conservative in the downgradient aquifer, and gypsum may only be precipitating locally. Concentrations of iron and manganese seem to be controlled by the precipitation of ferric oxide and hydroxides and rhodochrosite, respectively. Complete neutralization of mine drainage by carbonates is consistent with high concentrations of calcium (up to 470 mg/l) and magne-

sium (up to 563 mg/l) and also with high strontium concentrations of up to 3.08 mg/l, observed in groundwater downgradient from the pile. Hydraulic head profiles at two sites within the river bottom sediments indicate upward flow toward the river with large local differences in groundwater recharge. Water chemistry profiles in the river bottom sediments and geochemical modeling suggest conservative behavior of Na, Cl, and SO₄ and precipitation of Fe and Mn at the groundwater/river water interface. Mine drainage enters the Bierawka River and causes increasing sulfate concentrations. In contrast, concentrations of sodium and chloride in the Bierawka River decrease downgradient from the pile because water in the river upgradient from the pile is already highly contaminated by these species from the discharge of mining waters. Concentrations of Fe and Mn in the river water are low, as a consequence of the precipitation of Fe and Mn oxide and hydroxides. Direct geochemical modeling was able to reproduce measured concentrations of conservative species (e.g., Na, Cl, and SO₄), but errors for metals and Ba were relatively large. In addition, calculated P_{CO2} values in the river water are very high, suggesting that equilibrium with atmospheric P_{CO2} and P_{O2} has not been reached, and at least some reactions should be modeled as kinetic processes. High concentrations of Na, Cl, and SO₄ contribute to the contamination of the Odra River, which is joined by the Bierawka River

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farther downgradient, thus limiting the use of river water for recreation and other purposes.

Keywords Coal waste pile · Mine drainage · River sediments · River contamination · Equilibration with atmosphere

Introduction

Acid mine drainage (AMD) from sulfidic waste rock piles is a serious environmental problem, which has serious impacts on the environment including aquatic life and human health. The AMD has been studied in several countries around the world such as Canada (Lefebvre et al. 2001; Sracek et al. 2004; Stockwell et al. 2006; Salzsauer et al. 2005), Sweden (Stromberg and Banwart 1999; Linklater et al. 2005), Peru (Smuda et al. 2007), Russia (Gieré et al. 2003), and Australia (Ritchie 1994). The mine drainage waters typically have low pH and high concentrations of sulfate, iron, and other metals (Blowes et al. 2003). However, when the neutralization capacity of waste rock significantly exceeds its acid generation potential, the resulting pH is neutral with high concentration of sulfate but low concentrations of iron in the drainage waters (Younger et al. 2002). Under neutral and oxidizing conditions, iron precipitates as oxyhydroxides on the surface of pyrite grains, which further limits pyrite oxidation (Nicholson et al. 1990; Hossner and Doolittle 2003). Mine waters have a detrimental impact on aqueous environment because they frequently are highly mineralized and, in the case of low pH, concentrations of several metals are also high. Other potential contaminants include nitrate from N-based explosives, organic substances from leaching of coal, and radionuclides (Banks et al. 1997).

There is a hyporheic zone between an aquifer and a river, which is divided into a surface hyporheic zone with dominant river water and precipitation of manganese minerals and an interactive hyporheic zone with a variable percentage of groundwater and precipitation of Fe(III) minerals (Triska et al. 1989; Benner et al. 1995). Mine drainage may interact with river bottom sediments, and several additional processes

including sulfate reduction, ammonia oxidation, and adsorption/precipitation of metals may also take place (Gandy et al. 2007; Cravotta 2008). Application of mini-piezometers installed in river bottom sediments is an efficient method to determine the influx into river and to monitor the associated geochemical reactions (Cey et al. 1998; Conant 2004).

The Upper Silesian Coal Basin is located in the south of Poland. A large number of coal waste piles in the region produce relatively neutral or only slightly acidic drainage (Szczepańska and Twardowska 1999). Furthermore, mine water pumped from coal mines is discharged into surface water bodies, and its impact on environment is similar to that of waste piles. The source of mine drainage are residual Na–Cl brines in waste material and the oxidation of pyritic sulfur (content up to 1.83 wt.%) and organic sulfur (content up to 0.48 wt.%) in coal (Gzyl and Banks 2007). Besides pyrite, principal secondary minerals in coal waste were identified as Na-jarosite and gypsum. The most common ions in mine drainage are Cl^- and Na^+ with concentrations up to 70 and 40 g/l, respectively. Next contaminant is sulfate produced by the oxidation of pyritic and organic sulfur. Concentrations of iron and other metals are generally low due to high pH values. Concentrations of radium may be high (up to 390 kBq/l expressed as activity), but they are limited to low sulfate waters (Chalupnik et al. 2001). In waters with high sulfate concentrations, radium co-precipitates with barite.

The coal waste pile at Smolnica in the Gliwice region (Fig. 1) is about 20 m high, covers an area of about 130 ha, and contains a waste rock volume of about $13,845 \times 10^3 \text{ m}^3$ (Twardowska and Szczepańska 1995). The waste originates from the KWK coal mine in Szczygłowice and produces what is generally known as contaminated neutral drainage or more simply as mine drainage (MD) as a consequence of the high neutralization capacity of the waste rock material. MD mixes with background groundwater in the unconfined aquifer around and below the pile and then flows toward the Bierawka River located close to the southern slope of the pile. The river functions as a discharge boundary where the MD is diluted and undergoes further attenuation reactions.



Fig. 1 Geographic location of the Smolnica pile

The principal objectives of the study were to (1) identify the geochemical processes in the aquifer surrounding the Smolnica pile and in the Bierawka River, (2) identify the processes occurring within the river bottom sediments, and (2) evaluate the impact of MD from the pile on the shallow aquifer and the Bierawka River.

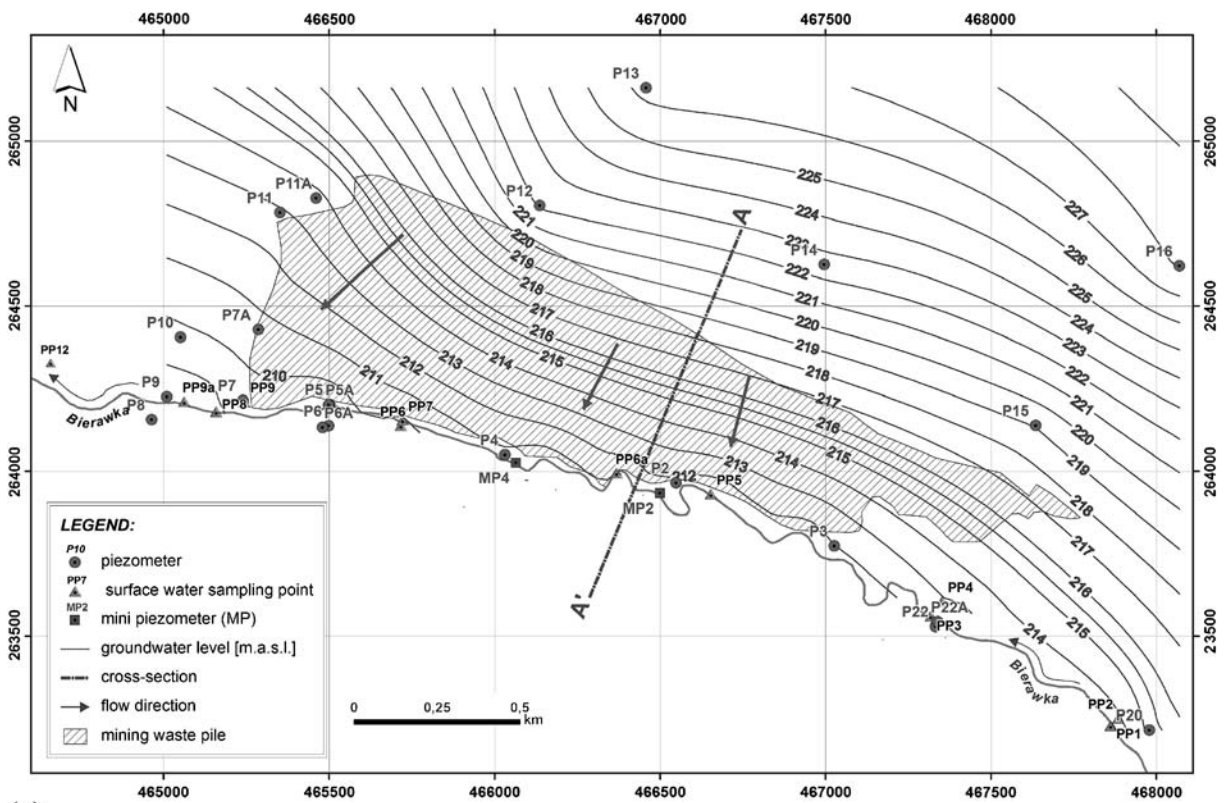
Site description and geological and hydrogeological characteristics

The pile material grain sizes vary from boulders of several decimeters diameter down to the clay fraction. Larger size fractions seem to have accumulated at the base of the pile as a consequence of transport by gravity. In the northern part of the pile (Fig. 2a), secondary recovery of coal from the waste was performed from 1988 to 1997 by the company Gwarex-Ryan Poland. This exploitation started in the NW section and continued toward the SE. The upper part of the waste has thereby been removed with the resulting increase in access of oxygen to the un-oxidized pyrite in the waste, which has accelerated the pyrite oxidation rate (POR). The pile is recharged by local precipitation of about 700 mm/year. The estimated fraction of precipitation recharging the pile is 0.4 (Kubica 2007).

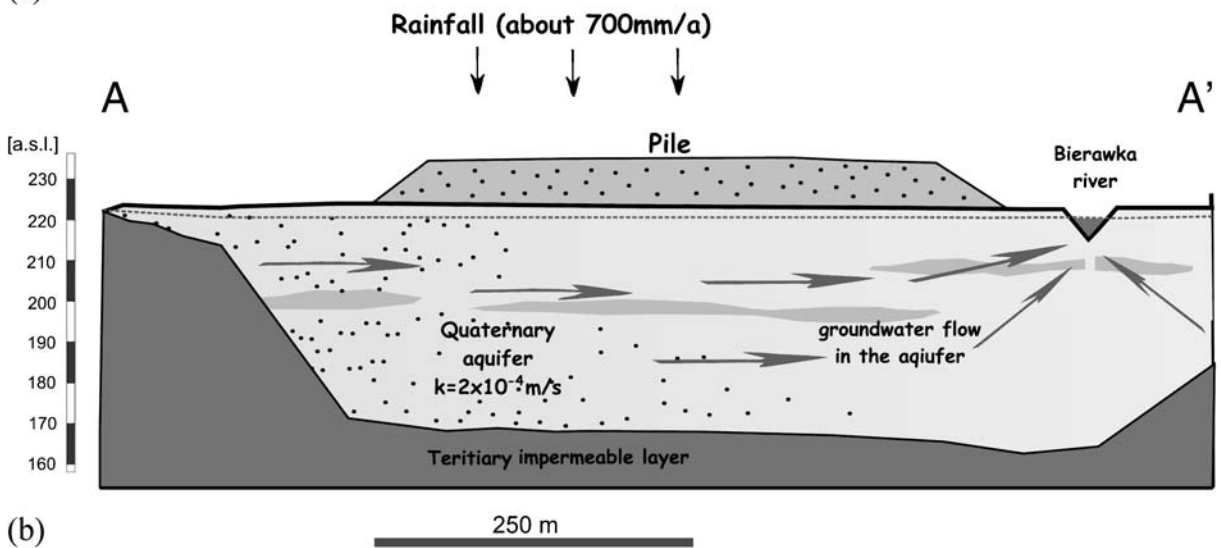
Tertiary sediments underlying the Smolnica site are >300-m thick and are composed of clays and marls. Quaternary sediments lie on top of the Tertiary formation, in direct contact with the waste rock (Fig. 2b). They were deposited on the irregular surface of Miocene clays. Their thickness is 6–10 m, and they are composed of sand mixed with silt and clay. A relatively continuous layer of clay and silt lies above the sandy layer. Sediments of the Bierawka River lying south of the pile are composed of sandy gravels and locally covered by clay and silt. Historically, the position of the Bierawka River was toward the north, which led to the deposit of sandy gravel sediments below the central zone of the pile. Indeed, the pile site was originally used for sand mining, which had formed a large open pit excavation. This pit was later filled by waste rock, which can be found below the current ground level.

Two aquifers are present at the site, which are of Tertiary and Quaternary ages. The Tertiary aquifer is composed of Pliocene sands and gravels and Miocene sandy gravels. They together form the usable groundwater aquifer (UGWA)–Kedzierzyn Trł, which is used as a water source in the villages of Sosnicowice, Chorynskowice, Smolnica, Ani Wielkie, and Kotlarna. This confined aquifer is recharged from outcrops around the Smolnica site. The top of the Tertiary aquifer was reached at a depth of 6.3 m in well BD-1 at the southwestern corner of the pile (Fig. 2a).

The Quaternary aquifer is defined as the UGWA “Gorna Odra,” which is unconfined and recharged directly by rain infiltration. The depth to water level is from 1.04 m (well P-20) to 5.2 m (well P-47). Due to the presence of coarse sands, the hydraulic conductivity is relatively high, from 2.20×10^{-6} to 3.71×10^{-4} m/s. Mean hydraulic gradients are 0.009 to the west and 0.0012 to the east of the site. The flow direction is toward the southwest where groundwater recharges the Bierawka River (Fig. 2a, b). Calculated average linear velocities are 0.2–0.3 m/day, but they can be much higher locally (>2.0 m/day at well PM-10 west of the pile, based on borehole dilution tests). South of the Bierawka River, groundwater flow is toward the northwest, i.e., the river is gaining water from both sides. There are no hydraulic and hydrogeochemical data available for the pile, and



(a)



(b)

Fig. 2 The Smolnica pile: **a** flow pattern and location of sampling points, **b** cross section

thus, they are inferred from testing and sampling of wells located in the surrounding aquifer. Hydrogeochemical characteristics of the Quaternary aquifer are discussed in the following chapters.

Flow in the aquifer surrounding the pile is toward the Bierawka River, which represents a local drainage base as an eastern tributary of the Odra River. There are no wells directly in the

pile, and reactions in the pile can be inferred only from the changes of dissolved concentrations between wells installed upgradient from the pile and downgradient from the pile on the bank of the Bierawka River (Kubica 2007). The aquifer is contaminated by MD with high concentrations of sulfate, chloride, and sodium. Although the Bierawka River is the principal recipient of contamination, it is already heavily contaminated upgradient from the pile from discharge of other mining waters, and thus concentrations of sodium, chloride, and sulfate in the river are already very high. Thus, care has to be taken to distinguish the impact of contamination from the Smolnica pile from other sources of contamination in the region.

Materials and methods

A total of 22 boreholes were drilled for the installation of piezometers (Fig. 2a), which were constructed using polyvinyl chloride (PVC) pipe with 2-in. ID. The lower part (about 1 m) of the PVC pipe was perforated, and the space around the perforated zone was filled with silica sand. Water samples from the piezometers were sampled by a short bailer, after removal of stagnant water. River samples were taken by a portable sampler at a depth of about one third of the water column in the river. No sampling points were available directly in the pile.

Field parameters taken on site were temperature, pH, Eh, electrical conductivity (EC), and dissolved oxygen (DO). The pH values were measured by a Radiometer Copenhagen PHM 80 with combination electrode C2401-7. Redox potential Eh was measured using a combined platinum electrode MC408Pt equipped with a calomel reference electrode. Field Eh values were corrected with respect to the E_{H_2} electrode. Values of EC and temperature were determined by an Aqualitic CD22 portable meter. Values of DO were determined by oxygen electrode.

Collected groundwater and river samples included (a) samples filtered using Sartorius 0.45- μ m filters and acidified by ultrapure HCl for cation and trace element analysis and (b) only filtered samples for anion analysis. Cation and metals were analyzed by AAS, anions were analyzed

using a Dionex ion chromatograph. Alkalinity was determined by titration with HCl, using the Gran plot to determine the titration end point.

Short mini-piezometers were driven by a hammer into the river bottom sediments at two sites (Fig. 1), at three different depth below the river bottom: 0.2, 0.4, and 0.6 m. Hydraulic head readings were taken, and after rapid removal of water mini-piezometers, the hydraulic conductivities were determined by the method of Hvorslev (Freeze and Cherry 1979). Water samples were treated and analyzed by the same methods as those used in the piezometers and river.

A multivariate statistical analysis was performed using the program PAST Hammer et al. (2001). Speciation calculations and geochemical modeling were performed using the program PHREEQC (Parkhurst and Appelo 1999).

Results

Geochemistry of the shallow aquifer

Data on the water chemistry in the shallow aquifer in the vicinity of the pile are provided in Table 1. Sampling point locations are shown in Fig. 2.

The pH values are in the range 4.5–7.4, with an average of 6.43, and a standard deviation of 0.58. All values except one (sample P8 with pH of 4.5) indicate neutralization of acidity produced by the oxidation of pyrite in the pile. In fact, the pH values of background samples P13 and P16 (5.9 and 6.0, respectively) are even lower than those of most MD samples.

The redox potential Eh values, corrected with respect to the H_2 electrode, are in the range 154–480 mV, with an average 245 mV and a standard deviation 16.6 mV. These values correspond to moderately reducing environments at the nitrate reduction level, but the Eh of a few samples at a lower range (<200 mV) correspond to a Fe(III)-mineral reduction level. Respective background values of Eh in upgradient wells P13 and P16 are 364 and 330 mV.

DO concentrations are in the range 1.4–7.9 mg/l, with an average of 4.09, and a standard deviation 0.43. This still indicates an oxic environment, and thus, there is a discrepancy between the

Table 1 Geochemistry of groundwater from piezometers in the shallow aquifer, Eh is in mV, concentrations are in mg/l

Parameter/well	pH	Eh	DO	Na	K	Ca	Mg	HCO ₃	Cl	SO ₄	NH ₄	Ba	Fe	Mn	Sr	Zn
P2	6.7	154	1.9	763	9	470	87	317	341	2644	0.67	0.026	148.4	7.43	0.968	0.07
P3	6.2	230	2.1	951	21	386	116	171	903	2180	1.03	0.053	26.4	10.32	1.13	0.05
P4	6.7	180	3.1	2606	115	399	563	878	507	3827	3.15	0.024	0.112	5.48	3.08	0.02
P5	6.6	210	2.6	6	1	28	4	107	7	42	0.29	0.049	0.112	0.17	0.075	0.03
P5A	6.3	190	2.8	736	22	354	164	336	320	2530	1	0.038	78	9.25	1.11	0.05
P6	6.8	272	7.2	9	3	33	5	98	10	99	0.25	0.102	0.1	0.25	0.089	0.04
P6A	6.9	180	1.4	5	1	25	4	79	6	34	0.31	0.058	0.2	0.16	0.071	0.02
P7	6.5	190	2.5	902	22	382	170	378	396	1950	1.71	0.024	0.112	5.67	1.4	0.06
P7A	7	209	5.9	493	36	289	233	427	334	1975	0.66	0.023	0.112	2.12	1.26	0.04
P8	4.5	480	6.7	5	2	20	4	24	11	120	0.1	0.075	0.2	0.28	0.088	0.23
P9	6.7	192	2.8	351	10	221	96	262	115	1256	0.86	0.03	0.112	2.55	0.816	0.05
P10	6.6	182	3.4	302	24	237	156	366	107	1492	1.19	0.004	0.112	6.05	0.912	0.04
P11	6.5	242	3	81	15	153	69	256	195	411	0.34	0.125	0.112	1.27	0.818	0.04
P11A	6.8	290	5.6	18	15	61	43	244	13	168	0.05	0.089	0.112	0.82	0.359	0.04
P12	6.2	331	4.9	9	3	32	6	37	15	80	0.09	0.044	0.112	0.124	0.168	0.06
P13	5.9	364	5.4	5	2	34	6	34	11	44	0.03	0.085	0.112	0.124	0.17	0.09
P14	6.1	247	5	6	2	25	7	24	9	78	0.39	0.078	3.3	0.22	0.134	0.07
P15	5.9	259	3.3	7	2	74	10	73	14	176	0.78	0.101	10.4	1.46	0.24	0.05
P16	6	330	7.9	9	3	56	8	31	24	73	0.03	0.118	0.112	0.124	0.16	0.02
P20	7.4	159	3.4	9	4	102	16	323	19	53	0.73	0.159	0.112	0.29	0.603	0.02
P22	7	234	1.5	4	2	40	5	122	9	22	0.06	0.043	0.112	0.39	0.124	0.04
P22A	6.1	281	7.5	5	3	21	6	40	4	56	0.33	0.061	0.2	0.29	0.082	0.37

DO values and some Eh values. However, redox disequilibrium between the O_2/H_2O redox couple and measured Eh values has frequently been observed (Stumm and Morgan 1996). In summary, the aquifer is too oxidizing for sulfate reduction, and ferric iron reduction is possible only in some samples.

Values of EC, which roughly correspond to the degree of mineralization, are in the range from 0.022 to 12.597 mS/cm, with an average of 2.26 mS/cm, and a standard deviation of 3.1 mS/cm. The most contaminated sample P4 also has the maximum value of EC.

Concentrations of Ca are highly variable, from 20 to 470 mg/l, average 154.9 mg/l, and standard deviation 154.9 mg/l. Respective concentrations in background wells P13 and P16 are 34 and 56 mg/l. On the other hand, concentrations in the most contaminated wells (on the basis of sulfate) P4 and P2 are 470 and 399 mg/l, respectively. This suggests that Ca is produced by the dissolution of carbonates during the neutralization of acidity produced by the oxidation of pyrite.

Concentrations of Mg also exhibit a considerable range from 4 to 563 mg/l, with an average of 80.8 mg/l and a standard deviation of 27.3 mg/l. Background concentrations in well P13 and P16 are 6 and 3 mg/l, respectively. They are much lower than background Ca concentrations, suggesting that Mg carbonates like dolomite are in the waste pile but not in the surrounding aquifer.

Concentrations of Na are in the range 4–2,606 mg/l, with an average of 331 mg/l, and a standard deviation of 129 mg/l. They seem to be linked to the flushing of brines initially present in waste material (Chalupnik et al. 2001). Background concentrations are about 5 mg/l (well P13). Concentrations of K are in the range from 1 to 115 mg/l (average, 14.4 mg/l; standard deviation, 24.5 mg/l). They also seem to be linked to the brine residuals in the waste.

Concentrations of bicarbonate are in the range from 24 to 878 mg/l (average, 210.3 mg/l; standard deviation, 42.9 mg/l). Bicarbonate is produced during AMD neutralization by carbonates. This is consistent with low background concentrations (34 mg/l in P13). A maximum concentration of 878 mg/l was found in the most contaminated well P4.

Sulfate concentrations are in the range from 22 to 3,827 mg/l (average, 877.7 mg/l; standard deviation, 1,147 mg/l). Sulfate is produced by the oxidation of pyrite, and there does not seem to be any geochemical sulfate attenuation process in the downgradient aquifer (see later). Background concentrations are around 44 mg/l (well P13).

Chloride concentrations are in the range 4–903 mg/l (average, 153.2 mg/l; standard deviation, 49 mg/l). They seem to be linked to the flushing of brines originally present in the waste rock material. Background concentrations are around 11 mg/l (well P13).

Concentrations of iron at this site are relatively low, in the range from 0.1 to 148.4 mg/l (average, 12.21 mg/l; standard deviation, 7.45 mg/l). This indicates that behavior of iron is less conservative than the behavior of sulfate because both contaminants are produced by the oxidation of pyrite. A principal parameter determining the behavior of iron is Eh because, at the close to neutral pH observed at this site, Fe(III) precipitates as oxides or hydroxides.

Concentrations of manganese are in the range from 0.12 to 10.32 mg/l (average, 2.49 mg/l; standard deviation, 0.7 mg/l). Manganese may be produced by the dissolution of ankeritic dolomite present in the rocks (Banks 2006). Once again, at this pH range, the principal factor governing Mn behavior is the redox potential Eh.

Concentrations of ammonia are in the range from 0.03 to 3.15 mg/l (average, 0.64 mg/l; standard deviation, 0.72 mg/l). This is in good agreement with moderately reducing Eh values and with low nitrate concentrations.

Concentrations of Sr are in the range from 0.71 to 3.15 mg/l (average, 0.630 mg/l; standard deviation, 0.711 mg/l). Strontium is commonly present in the structure of carbonates, and its increasing concentrations indicate a high carbonate dissolution rate in the zone affected by the oxidation of pyrite.

Concentrations of Zn are in the range from 0.02 to 0.37 mg/l (average, 0.068 mg/l; standard deviation, 0.08 mg/l). Zinc is generally present as Zn^{2+} and is adsorbed on Fe(III) oxides and hydroxides at moderately acidic and neutral pH conditions.

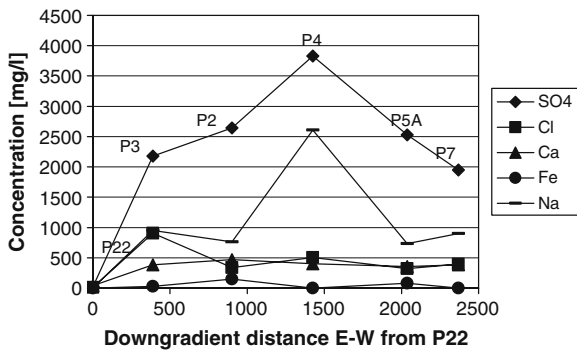


Fig. 3 Concentrations of selected species in wells along the Bierawka River

Barium has concentrations in the range from 0.004 to 0.159 mg/l (average, 0.064 mg/l; standard deviation, 0.04 mg/l). Concentrations of Ba in background groundwater are generally higher than in the groundwater contaminated by MD. This indicates dissolved Ba control by the precipitation of barium when sulfate concentration becomes high.

Selected species within the cross-section roughly aligned along the W–E direction (along the Bierawka River) are shown in Fig. 3. All wells, except the most eastern P22, are contaminated with sulfate, reaching a maximum of 3,827 mg/l in P4. However, the maximum Cl concentration is in P3 located about 1,040 m east of P4. This may be a consequence of more limited leaching at the pile zone or higher initial Cl concentrations in the waste material. Concentrations of Ca are around 400 mg/l, with a maximum of 470 mg/l in P2. Concentrations of Fe in the most contaminated well P4 is at detection limit, but its concentrations in wells P5A, P2, and P3 are significant, reaching 78, 148.4, and 26.4 mg/l, respectively. Since pH is close to neutral, the differences probably reflect more reducing conditions. The highest concentration of Na coincides with the maximum for sulfate in P4. Concentrations of Na are generally higher than those of Cl, but in well P3, these concentrations are similar.

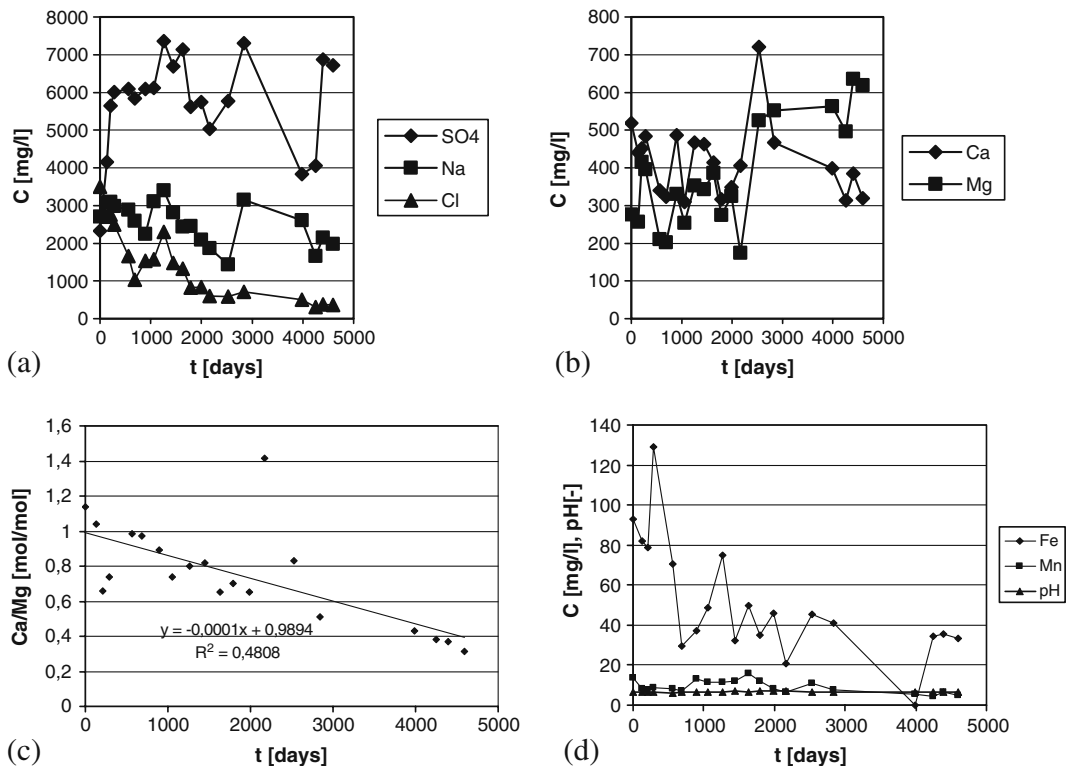


Fig. 4 Temporal concentration trends for P4: **a** SO₄, Na, Cl, **b** Ca, Mg, **c** Ca/Mg molar ratio, **d** Fe, Mn, pH

Temporal concentration trends

Temporal trends for the period 1994–2007 were studied at two highly contaminated wells P4 and P2 located between the pile and the Bierawka River. Results for selected species for P4 based on Kubica (2007) are in Fig. 4. From Fig. 4a, it is evident that the concentrations of sulfate and sodium exhibit similar behavior, and chloride concentrations decline. Since chloride is not adsorbed, it is flushed out of the porous media relatively quickly. On the other hand, after flushing of sulfate in the brine, there is a contribution of sulfate produced by the dissolution of pyrite. Sodium is present at exchange sites and is only slowly replaced by Ca and Mg produced by the dissolution of carbonates. In Fig. 4b, there is a trend of decreasing concentration of Ca and an increasing trend of Mg concentrations in time. This is probably caused by an increasing role of less soluble dolomite. This is

also supported by Fig. 4c, where the molar Ca/Mg ratio is initially >1.0 but later drops below 1.0. There are decreasing Fe concentrations in time in Fig. 4d.

There are three statistically significant linear trends at the highly contaminated site P4 (Sracek 2007); the trends are decreasing concentrations for Cl ($r^2 = -0.84$) and increasing concentrations for Mg ($r^2 = 0.77$) and increasing pH ($r^2 = 0.57$). This is in good agreement with the expected flushing of Cl and with the increasing role of dolomite dissolution. There is also a slightly increasing trend for sulfate ($r^2 = 0.13$) and a decreasing trend for Ca ($r^2 = -0.21$), but both trends are statistically insignificant.

Temporal concentrations for the less contaminated site P2, located east (upgradient) of site P4, are in Fig. 5. Development of sulfate, Cl, and Na concentrations seems to be similar to that at P4, but the decrease of Cl concentration is slower

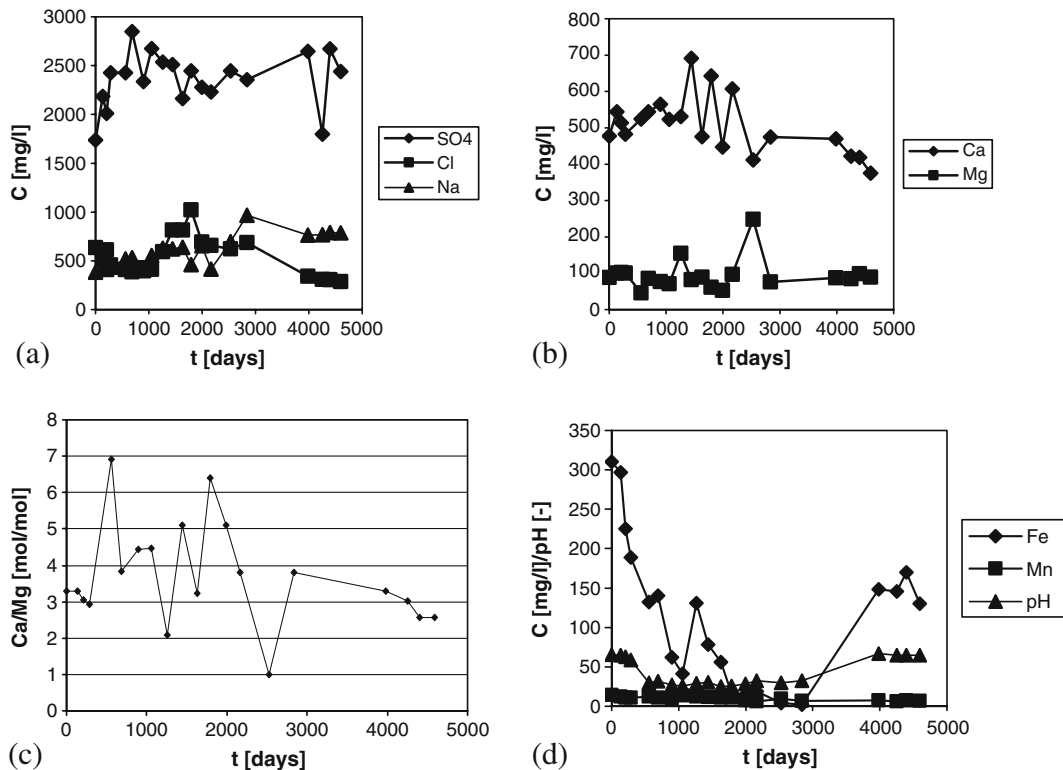


Fig. 5 Temporal concentration trends for P2: **a** SO₄, Na, Cl, **b** Ca, Mg, **c** Ca/Mg molar ratio, **d** Fe, Mn, pH, pH is exaggerated 10×

(Fig. 5a). The principal difference is in the Ca and Mg concentrations (Fig. 5b), where Ca concentrations are always higher than Mg concentrations. This is also consistent with the molar Ca/Mg ratio (Fig. 5c), which is always >1.0 . This suggests that dolomite is less abundant in the adjacent pile material than at P4. As shown in Fig. 5d, Fe concentrations were initially high, then decreased and returned to initial concentrations later. The same trends were observed for Mn. Values of pH decreased temporarily, probably as a consequence of coal recovery, and then increased again.

In contrast to site P4, the temporal linear trends are less statistically significant, with the highest r^2 value of -0.509 for Ca (Sracek 2007). Trends for sulfate ($r^2 = 0.147$), Mg ($r^2 = 0.083$), and pH ($r^2 = 0.262$) are positive; trends for Cl ($r^2 = -0.133$) and Fe ($r^2 = -0.301$) are negative.

Geochemistry of the Bierawka River

The MD with high concentrations of sulfate, chloride, sodium, iron, and manganese is entering the Bierawka River, which is already strongly contaminated by mining water discharge from underground coal mines located upgradient from the Smolnica pile. Selected water chemistry parameters for river water and for the P6 well located at the uncontaminated left (south) side of the Bierawka River are shown in Table 2. Concentrations of major species are also plotted vs. distance in Fig. 6. Water discharge measurements by the velocity–area method were performed at profile PP2 located east of the pile and at profile PP12 located west of the pile (Fig. 2).

River water is already strongly contaminated at profile PP2 upgradient of the pile, where concentrations of sodium, chloride, and sulfate are already very high. Also notable is the concentra-

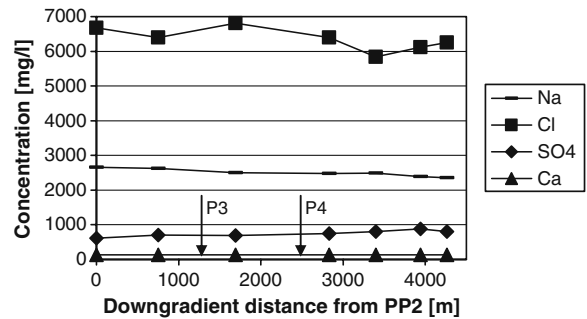


Fig. 6 Concentrations of major species in the Bierawka River

tion of ammonium ions. At profile PP12, the concentrations of sodium and chloride slightly decrease, and the concentration of sulfate increases by about 30%. Concentrations of Fe and Mn increase only slightly, and concentrations of strontium and ammonium ions decrease. Values of pH downgradient of the pile decrease, suggesting that river water is not equilibrated with atmospheric P_{CO_2} . Concentrations of major species along the river profile are shown in Fig. 6.

It is evident that chloride concentrations increase close to well P3, which contained the highest groundwater chloride concentrations (903 mg/l). Chloride concentrations in the river decrease beyond well P4, where the chloride concentration in groundwater is only 507 mg/l. As stated earlier, principal chloride source in the river water is mine water discharge. Contribution from the pile plays some role, but water recharge from the pile has generally a diluting effect. There seems to be a slight downgradient decrease in sodium concentration and increase in sulfate concentration. Concentrations of sulfate in river water increase downgradient from well P4, which has a maximum sulfate concentration of 3,827 mg/l. On the other hand, the concentration of calcium in river water is almost constant.

Table 2 Chemistry of river water at initial profile (PP2), final profile (PP12) and uncontaminated groundwater (well P6), and river discharge; concentrations are in mg/l, discharge Q is in m^3/s

Parameter/point	pH	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	Fe	Mn	Ba	Sr	NH ₄	$Q(m^3/s)$
PP2	7.48	138	135	2656	54	342	609	6671	0.66	0.25	0.109	3.40	2.37	0.851
PP12	6.97	129	123	2361	45	342	800	6254	1.19	0.40	0.087	2.86	0.059	0.946
P6	6.8	33	5	9	3	98	99	10	0.1	0.25	0.102	0.09	0.25	n.a.

n.a. not applicable

Mass fluxes for profiles PP2 and PP12 were calculated as a product of discharge and concentration (Sracek 2007). When the mass flux decreases or remains constant between profiles and the concentration decreases, the concentration change is caused only by dilution. When mass flux for a species increases, there is a source for that species. At this site, there is a slight 1.2% decrease of sodium mass flux between the profiles. This may have been caused, for example, by cation exchange on the river bottom sediments. On the other hand, the mass flux for chloride increases in spite of decreasing chloride concentrations by 4.2%. This means that the dilution rate is slower than the input of chloride from the contaminated aquifer at the right side of the river. However, both changes are within the margin of error for the applied methods because the velocity–area discharge measurement alone has an error of about 15% (Cey et al. 1998). Mass flux for sulfate increases by 46%, consistent with expected input from the contaminated aquifer. Mass fluxes for Ca and Mg increase by 3.1% and 1.3%, respectively, but these values are again within the margin of error (Sracek 2007).

Flow and pore water chemistry in river sediments

Profiles of hydraulic head and hydraulic conductivity in river bottom sediments are shown in Figs. 7 and 8, respectively. The hydraulic gradients in the river sediments are always upward, e.g.,

shallow aquifer water is recharging the Bierawka River. The hydraulic gradient at site MP2 is from 0.05 to 0.07. At site MP4, the hydraulic gradient increases with depth where it reaches 0.275, but decreases to 0.075 close to the river bottom. This is consistent with a layer of low permeability located at the site at about the 0.6-m depth. At both sites, the hydraulic conductivity increases upward. Calculated specific discharges at MP2 and MP4 are 4.18×10^{-6} and 2.14×10^{-6} m/s, respectively. This is consistent with the more sandy character of sediments at MP2 site.

Assuming a wetted cross-section in the river of about 5 m² and interpolated discharge in the river close to site MP4 of 0.895 m³/s, the discharge in the river per 1 m² is 0.180 m/s. The input of groundwater is about 0.0023% and 0.0012% of total river discharge at sites MP2 and MP4, respectively. Thus, the mixing ratio is from about 500:1 to 1000:1, suggesting that water chemistry is completely dominated by the river water.

When total groundwater input between velocity–area measurement profiles PP2 and PP12 (Fig. 2, Table 2) is taken into account, for an estimated wetted area of river sediments of 32,400 m², the calculated groundwater discharge into the river is 0.135 m³/s, based on the data from site MP2, and 0.069 m³/s, based on the data from site MP4. This compares well with groundwater input based on the velocity–area method equal to 0.095 m³/s, which is bounded by these two values. When a geometric mean of both specific discharge values equal to 2.99×10^{-6} m/s is

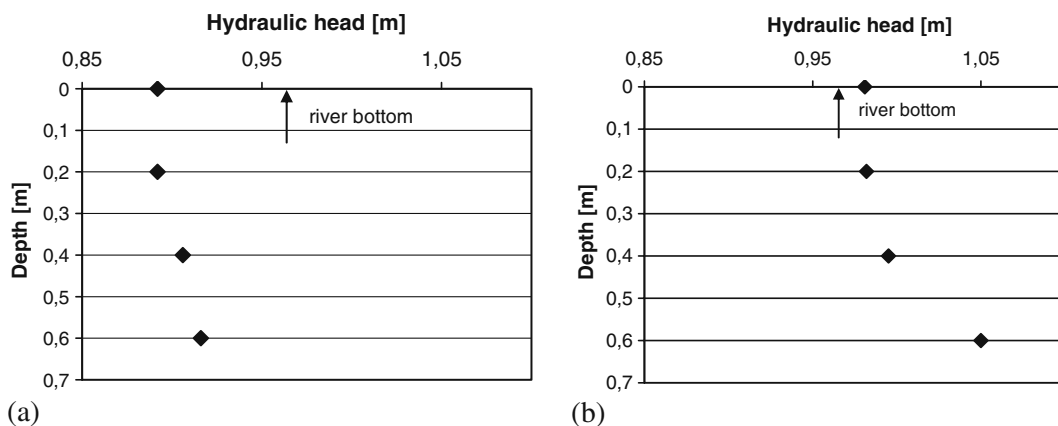


Fig. 7 Hydraulic head profiles in river sediments: a site MP2, b site MP4

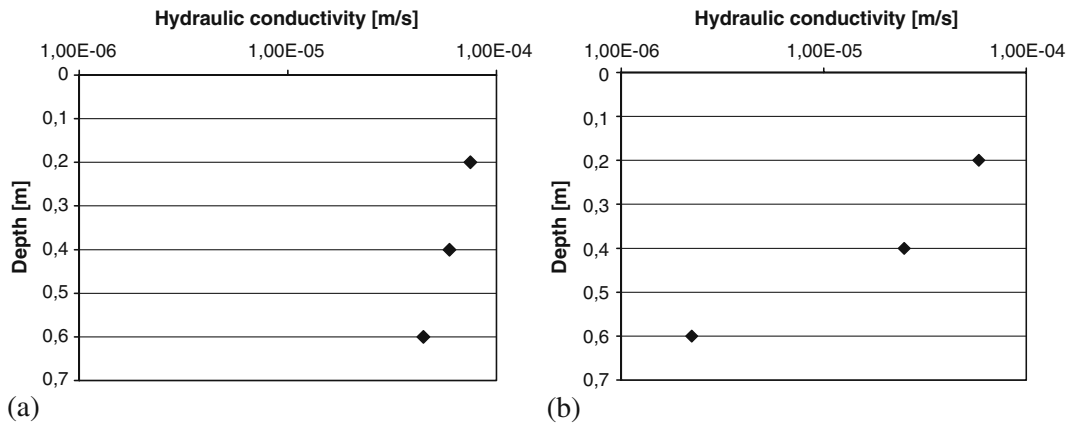


Fig. 8 Hydraulic conductivity profiles in river sediments: **a** site MP2, **b** site MP4

used for calculation, the calculated discharge is 0.0969 m³/s, i.e., the difference is only about 2%.

Profiles of pore water concentrations for selected species are shown in Fig. 9. Values of pH were relatively constant, in the range from 6.6 to 7.0. The same holds for the redox potential Eh, which varied from +160 to 225 mV. The concentration profiles in river sediments reflect the differences between the shallow aquifer and the river and also between different wells in the shallow aquifer. For example, at well P4 close to site MP4, concentrations of Na, Cl, and sulfate are higher than at well P2 close to site MP2. The differences are also observed at both sites in the deepest minipiezometers (Fig. 9a, b), but the differences are smeared close to the river bottom as a consequence of mixing with river water. There is a big difference in Fe concentrations between both sites, which reaches more than 100 mg/l at site MP2. This is consistent with much higher Fe concentrations in the neighboring piezometer P2 compared to the piezometer P4 (Table 1), attributed to more reducing conditions in this zone of the shallow aquifer. Concentrations of Mn are comparable at both sites, reaching about 10 mg/l. Speciation calculations showed that equilibrium is not reached with respect to any carbonate or sulfate mineral (Sracek 2008). This means that the principal ions behave conservatively and are attenuated only by dilution in the river. On the other hand, the pore water is supersaturated with respect to Fe(OH)₃(a) and goethite, FeOOH, and also with respect to Mn(II) with the min-

eral rhodochrosite, MnCO₃ (Sracek 2008). Thus, Fe and Mn may be attenuated by precipitation, but dilution by river water plays a principal role. Profiles for the nitrogen species indicate not only relatively significant loading of ammonia, but also a highly variable loading of nitrate.

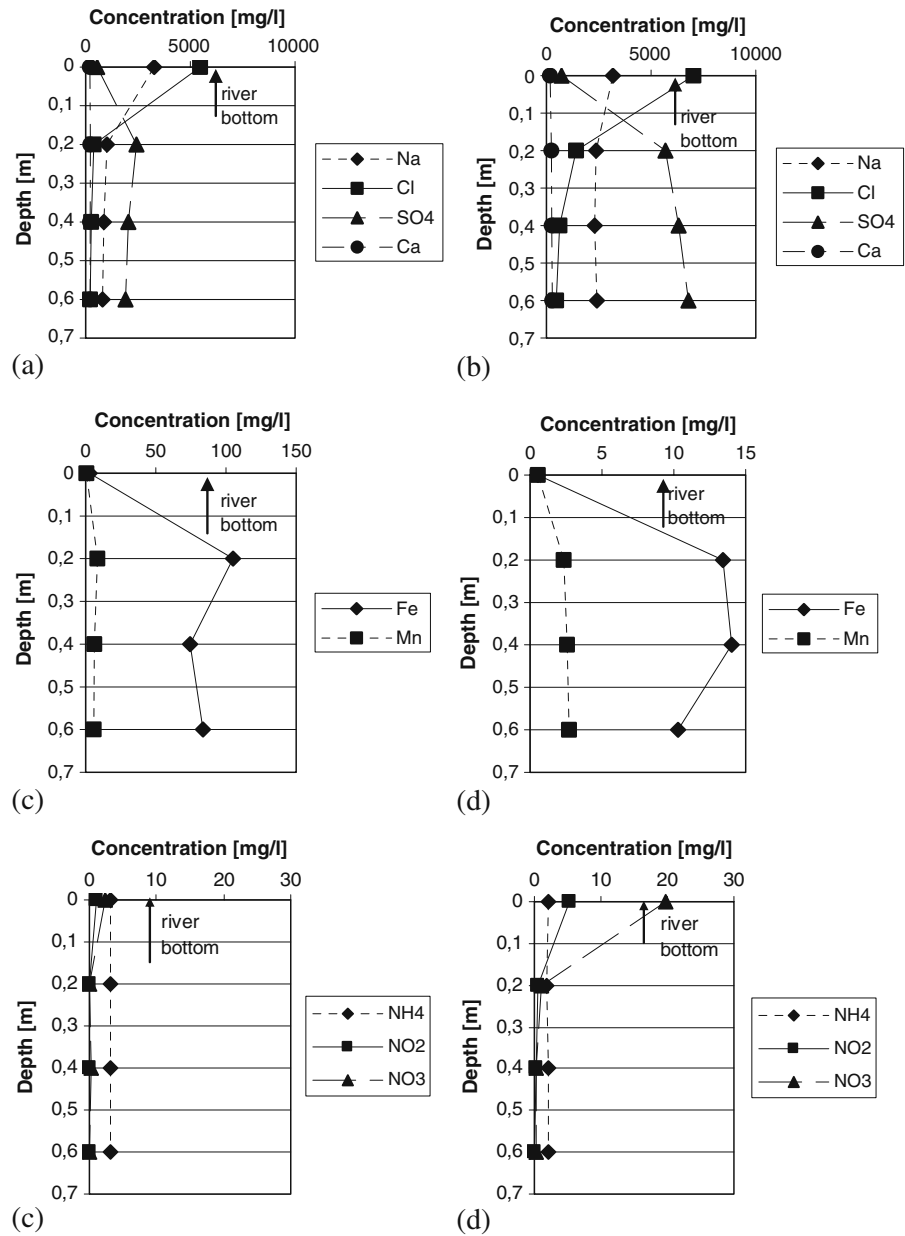
Bivariate plots, speciation modeling, and multivariate statistics

The plot of Ca vs. SO₄ for groundwater samples from the shallow aquifer is shown in Fig. 10a. The r^2 value is high (0.901), and the sulfate concentration is increasing even at high Ca concentrations. This indicates that there is no precipitation of gypsum even in samples with high sulfate and Ca concentrations. The only exception is sample P4, in which precipitations of gypsum is possible.

The plot HCO₃ vs. Ca (Fig. 10b) indicates an intermediate correlation ($r^2 = 0.546$), and the plot of HCO₃ vs. Mg (Fig. 10c) indicates a high correlation ($r^2 = 0.871$). This is consistent with the expected important role of calcite and dolomite dissolution in AMD neutralization. More limited correlation for Ca is probably caused by the precipitation of gypsum directly in the pile.

In the plot of Cl vs. Na (Fig. 10d), the correlation is intermediate ($r^2 = 0.554$). This may be caused by less conservative behavior of Na, caused probably by cation exchange. The plot of Sr vs. Ca (Fig. 10e) shows a relatively good correlation between both species ($r^2 = 0.678$), suggesting input

Fig. 9 Profiles in pore water sediments for: **a** site MP2: Na, Ca, Cl, and SO₄, **b** site MP4: Na, Ca, Cl, and SO₄, **c** site MP2: Fe and Mn, **d** site MP4: Fe and Mn, **e** site MP2: NH₄, NO₂ and NO₃, and **f** site MP4: NH₄, NO₂, and NO₃



of Sr from dissolution of carbonates. On the other hand, there is a negative correlation between Ba and SO₄ (Fig. 10f), indicating the control of Ba concentrations in high sulfate water by the precipitation of barite.

Speciation modeling was performed using the program PHREEQC (Parkhurst and Appelo 1999). The saturation indices calculated by the program are defined as $SI = \log(IAP/K_{sp})$, where

IAP is the ion activity product and K_{sp} is solubility product at a given temperature, taken from the literature. Positive SI values indicate supersaturation with respect to a mineral; negative SI values indicate undersaturation with respect to a mineral.

Saturation indices SI (Fig. 11a) for gypsum are negative, but indices for some samples are close to equilibrium. There are negative and very negative respective SI values for calcite

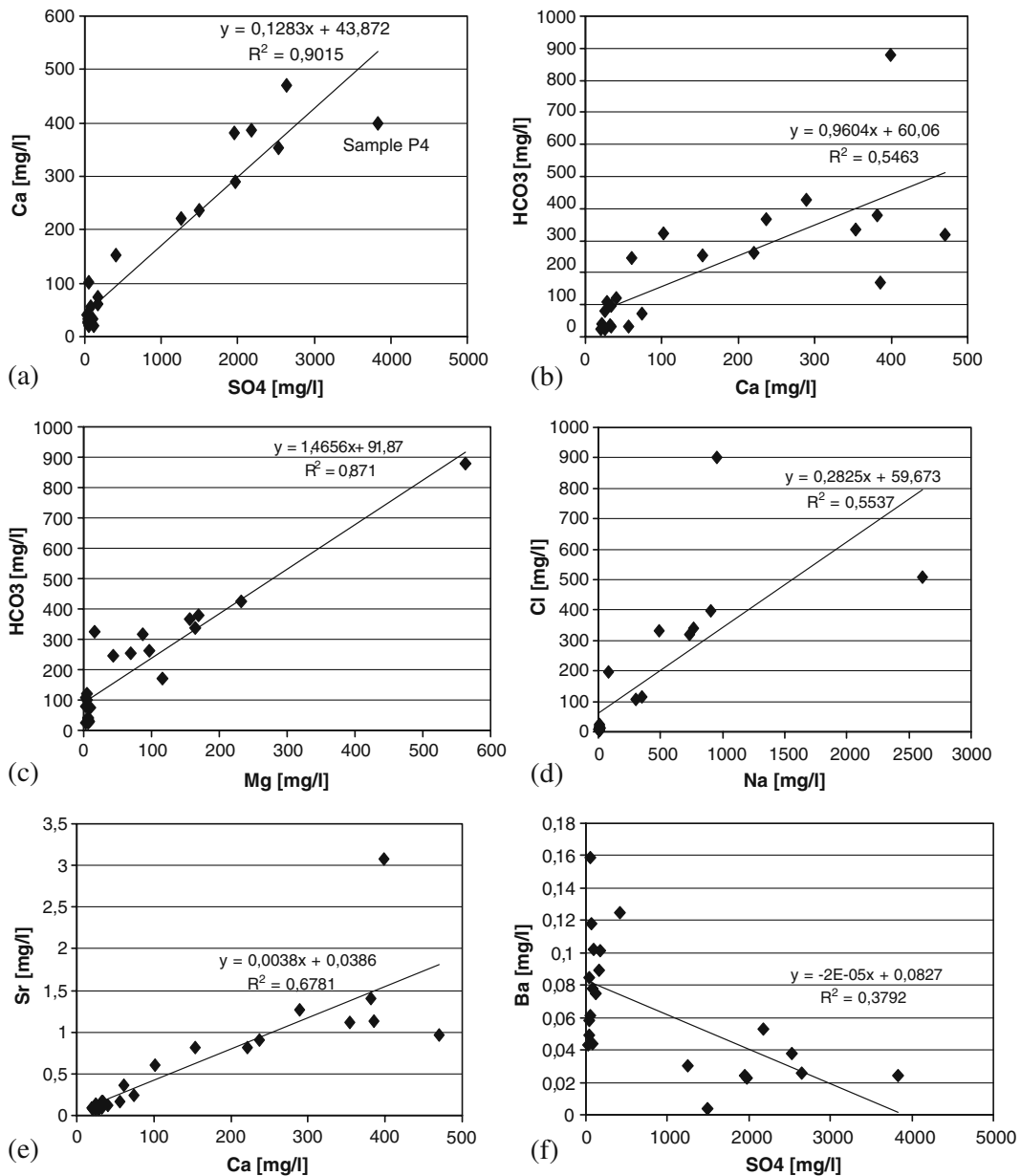


Fig. 10 Bivariate plots for samples from shallow aquifer: **a** Ca vs. SO₄, **b** HCO₃ vs. Ca, **c** HCO₃ vs. Mg, **d** Cl vs. Na, **e** Sr vs. Ca, **f** Ba vs. SO₄

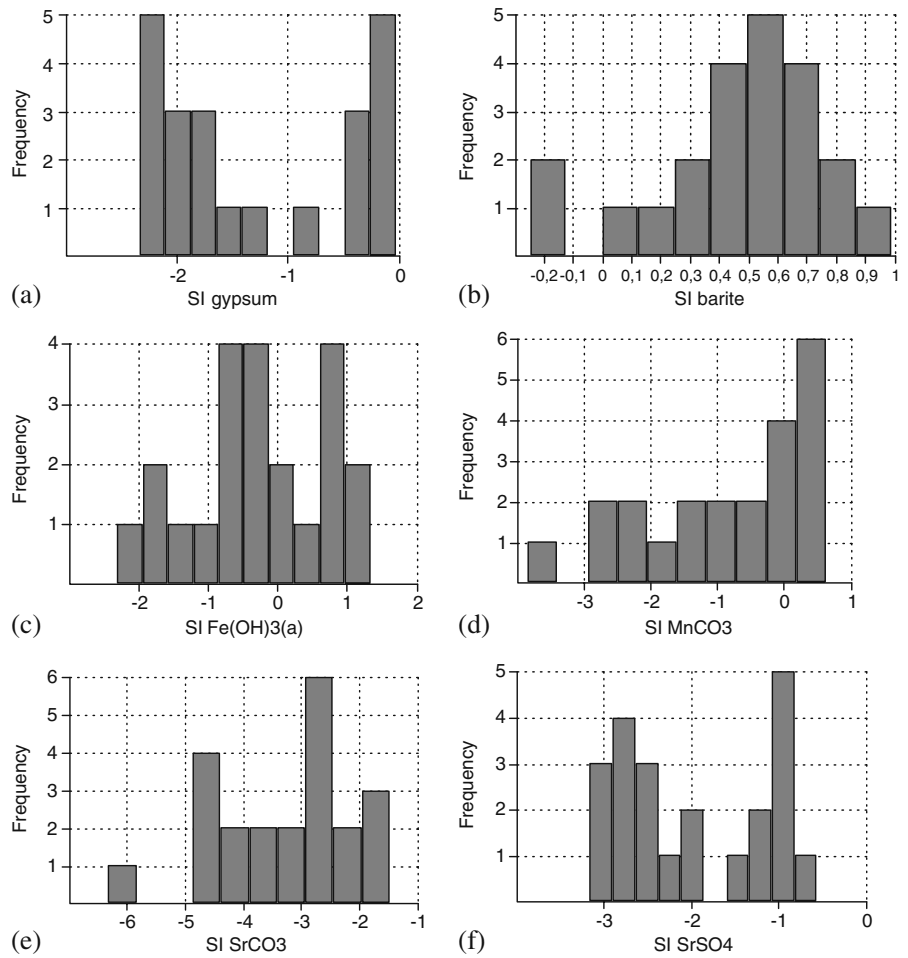
(average, -1.33) and dolomite (average, -3.01 ; not shown).

All samples but one are supersaturated with respect to barite (Fig. 11b), suggesting that this phase controls dissolved barium concentrations. Values of SI for amorphous ferric oxide, Fe(OH)₃(a), are in a wide range (Fig. 11c), suggesting that iron may be precipitating in

some samples. Furthermore, some SI values for rhodochrosite, MnCO₃ (Fig. 11d), are positive, indicating the possibility of manganese precipitation in samples with high alkalinity.

Values of SI for the strontium minerals strontianite, SrCO₃, and celestite, SrSO₄, (Fig. 11e, f, respectively) are all negative, suggesting that Sr may behave conservatively at the site. However,

Fig. 11 Results of speciation calculations for groundwater samples: **a** gypsum, **b** barite, **c** Fe(OH)₃(a), **d** MnCO₃, **e** SrCO₃, **f** SrSO₄



Sr may co-precipitate with barite (Cravotta 2008), but no data on a possible solid solution with barite are available.

In background samples (P13, P16), Fe(II) is present as the free ion Fe²⁺ and as the FeHCO₃⁺ complex. The same applies for Mn(II), which is present as Mn²⁺ and MnHCO₃⁺. Fe(III) and

Mn(III) are present as Fe(OH)₂⁺ and Mn(III). Most of the calcium and magnesium are present as free ions Ca²⁺ and Mg²⁺. In highly contaminated sample downgradient of the pile (P2, P3, and P4), Fe(II) is present as the free ion Fe²⁺ and as the FeSO₄⁰ complex. The same applies for Mn(II), which is present as MnSO₄⁰. Fe(III) and

Table 3 Results of speciation calculations for river water

Parameter/profile	SI _{calcite}	SI _{dolomite}	SI _{gypsum}	SI _{Fe(OH)3(a)}	SI _{goethite}	SI _{manganite}	SI _{barite}	SI _{strontianite}	SI _{celestite}	log PCO ₂
PP2	0.12	0.49	-1.23	3.11	8.69	4.98	0.60	-0.99	-1.13	-2.11
PP3	-0.26	-0.28	-1.17	2.97	8.55	4.21	0.64	-1.37	-1.08	-1.17
PP5	-0.40	-0.57	-1.17	3.02	8.60	4.02	0.63	-1.53	-1.10	-1.17
PP6	-0.35	-0.48	-1.13	3.22	8.82	4.28	0.70	-1.51	-1.09	-1.13
PP8	-0.36	-0.48	-1.10	3.27	8.85	4.27	0.70	-1.50	-1.03	-1.10
PP10	-0.07	0.09	-1.08	3.39	8.97	4.84	0.73	-1.23	-1.03	-1.08
PP12	-0.41	-0.60	-1.12	3.12	8.7	4.18	0.68	-0.57	-1.06	-1.59

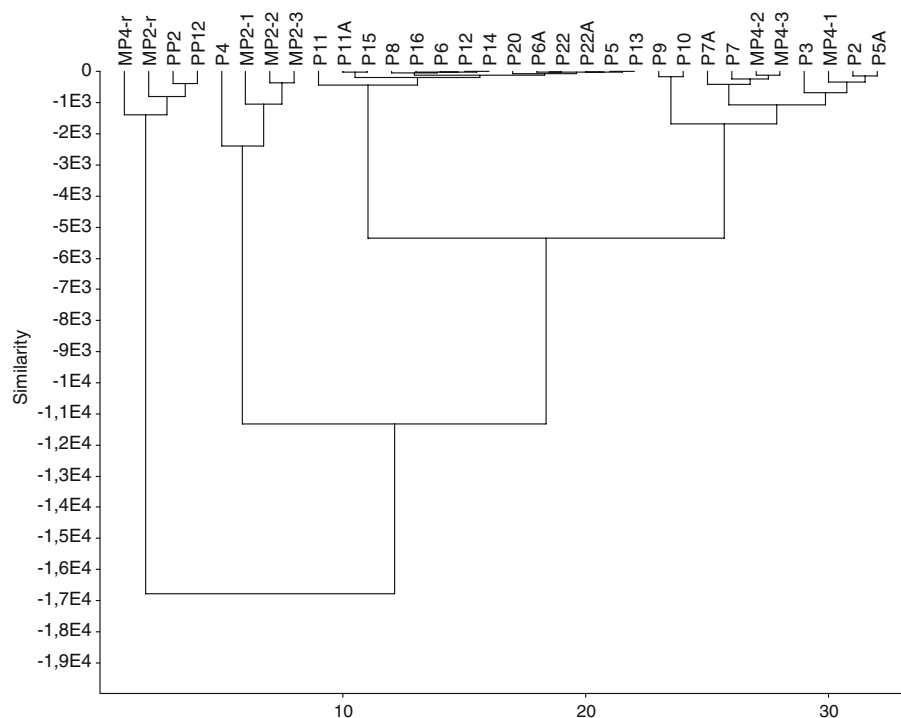
Values in italics refer to supersaturation

Mn(III) are present as $\text{Fe}(\text{OH})_2^+$ and Mn^{3+} . Calcium and magnesium are present as free ions Ca^{2+} and Mg^{2+} , but CaSO_4^0 and MgSO_4^0 complexes are also important (up to 40% of the respective total concentrations).

Selected results of geochemical speciation modeling for river water samples are in Table 3. The modeling was performed with equilibration of samples with atmospheric $\log P_{\text{O}_2} = -0.68$ because no Eh values or analytical speciation of redox sensitive species were available for the river. Samples in the background profile PP2 are supersaturated with respect to calcite and dolomite, but most samples located downgradient, and which are affected by mining drainage, are undersaturated with respect to these minerals. However, sample PP8 is close to saturation with calcite and is supersaturated with respect to dolomite. This means that carbonate minerals may precipitate from some samples at least. All samples are undersaturated with respect to gypsum, and sulfate seems to behave conservatively in the river.

All samples of river water are supersaturated with respect to Fe(III) minerals, Mn(IV) minerals and barite, suggesting that the precipitation of these minerals may control the concentrations of dissolved Fe, Mn, and Ba. All river water samples are undersaturated with respect to Sr minerals. Some notable features are the high calculated values of $\log P_{\text{CO}_2}$ (background value -2.11 and downgradient values up -1.08 for sample PP10), confirming that river water is not at equilibrium with atmospheric P_{CO_2} , which is equal to $10^{-3.5}$ atm due to continuous input of carbonate species produced by neutralization reactions in the pile. Carbon dioxide probably degases much further downgradient, assuming there is no more significant input of dissolved carbonate species from groundwater. Values of redox potential Eh calculated from the N(-III)/N(V) couple (e.g., from NH_4 and NO_3) were in the range from 0.347 V (PP2) up to 0.386 V (PP8). This suggests strong redox disequilibrium with the $\text{O}_2/\text{H}_2\text{O}$ couple and only slows oxidation of ammonia to nitrate in the rivers.

Fig. 12 Results of hierarchical cluster analysis (HCA) for shallow aquifer samples, selected river samples, and minipiezometer profiles samples (see text for discussion)



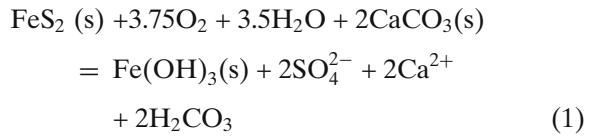
The multivariate statistical method of hierarchical cluster analysis performed in Ward’s mode (Hammer et al. 2001) was run for the groundwater samples from the shallow aquifer, selected samples from the river, and samples from the profiles in river bottom sediments. Results are shown in Fig. 12. There are four principal clusters. The left cluster includes river samples (PP2, PP12, MP2-r, and MP4-r) strongly contaminated by Na and Cl. The second cluster from the left includes the most contaminated well P4 and samples at minipiezometer profile MP2. These samples have higher concentrations of Na, Cl, and SO₄ than samples from profile MP4, probably due to higher permeability of sediments and rate of advective loading at this site. Upgradient background swells like P13 and P16, which are together with less contaminated wells P8 and P12, P6A, P15, P20, etc., are in the third cluster from the left. The last cluster at the right includes highly contaminated wells like P2, P3, etc., which are located directly downgradient from the pile and receive the principal contaminant load. In these wells, concentrations of Na and SO₄ are much lower than in the most contaminated well P4. Wells P7, P7A, P9, and P10, which are also in this cluster, are located close to the western margin of the pile. On the other hand, wells P22 and P22A located close to eastern margin of the pile are in the third cluster with less contaminated wells, thus indicating a more limited impact of contamination. This is consistent with the general direction of groundwater flow from NE to SW.

Discussion

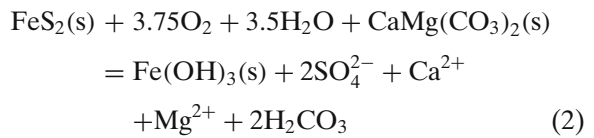
The background groundwater in the shallow aquifer, represented by wells P13 and P16 (Fig. 2), is of Ca-SO₄-HCO₃ type and is undersaturated with respect to calcite, dolomite, and gypsums. Values of pH are slightly acidic (around 6.0), and the redox potential Eh (330–370 mV) indicates moderately reducing conditions. Concentrations of Ba are from 0.38 to 0.66 mg/l, which are controlled by equilibrium with barite. Concentrations of Fe and Mn are low, close to the detection limit.

Within the pile, there is oxidation of pyrite by oxygen in the presence of water coupled to the

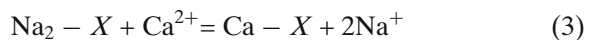
dissolution of calcite and precipitation of ferric hydroxide. The global equation is



Another neutralization mineral is dolomite. The neutralization reaction with dolomite is



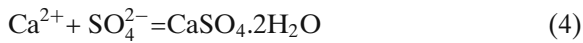
Both calcite and dolomite neutralize acidity, produced by the oxidation of pyrite, but dissolution of calcite is kinetically faster. The extent of both reactions can be estimated from Ca/Mg molar ratios in the downgradient wells. The ratios in wells P2, P3, and P4 are 3.28, 2.02, and 0.43, respectively. The ratio in P4 is close to the ratio 0.5 in dolomite, but ratios for P2 and P3 are much higher. This may be influenced by the fact that a part of both Mg and Ca may originate from leaching of the brine solution originally present in the waste material. In addition, Na originates from the brine, which is initially present in the waste material. At the beginning of the leaching and neutralization processes, Na is present on cation exchange sites, and the input of Ca from the dissolution of carbonates results in a slow release of Na:



where X indicates exchange sites. In contrast, chloride from the initial brine is present only in the pore water and, thus, is released much faster than Na.

Dissolution of Mg silicates, like muscovite and chlorite observed by Sracek et al. (2004), is insignificant under near neutral pH conditions

(Blowes et al. 2003). High concentrations of calcium and sulfate in water may result in the precipitation of gypsum,

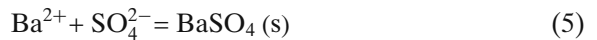


Saturation indices for gypsum, even in the most highly contaminated downgradient wells, are negative (Fig. 11a), but they are close to equilibrium in the strongly contaminated wells P2, P3, and P4. It seems that precipitation of gypsum is not an important process in the unconfined aquifer between the pile and the Bierawka River. However, gypsum precipitation probably takes place directly in the pile where data on pore water chemistry are not available.

Water resulting from the above reactions and sampled in wells downgradient from the pile have close to neutral pH (values, 6.2–6.7), reducing Eh (180–230 mV), low concentration of iron and high concentration of sulfate, calcium, and magnesium. Most of the iron is immobilized in Fe(III) minerals precipitating on the surface of pyrite already in the pile. The coating of reactive pyrite surfaces may result in decreasing POR due to increasing resistance to the diffusion of oxygen, (Nicholson et al. 1990; Hossner and Doolittle 2003). Concentrations of other metals are low, for example, low pH samples from P8 have only 0.23 mg/l of zinc. This is consistent with adsorption of positively charged metal ions at the pH range (Langmuir 1997).

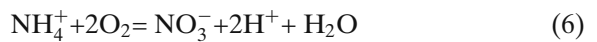
Since the waste contained residual brine with high Na and Cl concentrations, concentrations of Na and Cl in groundwater downgradient of the pile are also high. Manganese probably enters the water from the dissolution of Mn carbonates like ankerite $\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$, which may precipitate as rhodochrosite in high-alkalinity water. Calcite frequently contains Sr as an accessory, and samples with high Ca concentrations also have high Sr concentrations. Speciation calculations suggest that Sr behaves conservatively (assuming no co-precipitation with barite) and, thus, can be used to estimate the extent of neutralization. A maximum Sr/Ca molar ratio of 0.00353 was found in the most contaminated well P4. Values in wells P2 and P3 were 0.00094 and 0.0013, respectively.

When water from the pile with high sulfate concentrations recharges the underlying aquifer, precipitation of barite takes place,



Thus, concentrations of Ba in wells downgradient from the pile are suppressed, in spite of the probable input of additional Ba from the pile.

Leaching of the pile also results in high concentrations of the ammonia ion, NH_4^+ , which is originally present in brines. Ammonia concentrations reach 3.15 mg/l in P4 and 1.71 mg/l in P7. Concentrations of NH_4^+ are high in low Eh samples (Table 1). In more oxidizing environments, ammonia is oxidized to nitrate,



This reaction produces acidity, but its contribution to acidity is negligible compared to the oxidation of pyrite and is also neutralized by abundant carbonates.

In summary, groundwater in the shallow aquifer wells downgradient of the waste pile has close to neutral pH, moderately reducing Eh, and high concentrations of sulfate, bicarbonate, calcium, and magnesium. Concentrations of sodium and chloride are also high. In contrast, concentrations of metals like iron, manganese, and zinc are low, as are concentrations of barium. Concentrations of ammonia are higher in some wells, depending on redox conditions. In groundwater, both chloride and sulfate can be considered as conservative contaminants because equilibrium with respect to gypsum is not reached in most samples and the aquifer is too oxidizing for reduction of sulfate.

Direct geochemical modeling of the geochemical evolution in the Bierawka River has been performed in batch mode. Initial water was represented by sample PP2. The inflow of groundwater to the river, which was assumed equal to the difference in discharge between PP2 and PP12 (Table 2) obtained by the velocity–area method (here, 0.095 m³/s), was then divided by 2, assuming equal inflow into the river from the contaminated right side and uncontaminated left side (e.g., 0.0475 m³/s from each side). A groundwater sample from well P6 (Table 2) was used to

represent groundwater chemistry from the left side of the river, while the right side of the river was represented using the flow area-weighted average of concentrations in groundwater from wells located on the right bank of the Bierawka River. The groundwater inflow was mixed with the river water in a 9:1 ratio based on river discharge measurements, assuming perfect mixing in the river.

Two simulations were performed. The first simulation was a water mix equilibrated with $\log P_{O_2} = -0.68$, and precipitation of calcite, goethite, $Fe(OH)_3(a)$, manganite, and barite was allowed when supersaturation with respect to these minerals was reached. Initial equilibration with atmospheric CO_2 ($\log P_{CO_2} = -3.5$) was rejected because it would have resulted in a very high pH (around 8.2). The second simulation was performed only for conservative mixing (no precipitation of minerals was allowed). Results of both simulations are provided in Table 4.

In the first row, the calculated concentrations at profile PP12 for the reactive case, scenario (a), are shown. In the second row, there is a difference between the calculated and measured concentrations on this profile (see Table 2 for measured concentrations). A positive sign indicates higher calculated concentrations, while a negative sign indicates lower calculated concentrations. There is an excellent agreement for conservative species Na and Cl (respective errors are +4.5% and -2.5%). On the other hand, the error for sulfate is relatively large (about -16.4%). This was probably caused by additional groundwater sulfate input between monitoring wells, which was not accounted for in the modeling. Errors for Ca, Mg, Sr, and pH are still acceptable. Very large errors were found for Fe and Mn, which could not be evaluated quantitatively because the calculated Fe and Mn concentrations were almost zero. This has been caused by equilibration of the river water with atmospheric P_{O_2} followed by the precipitation of Fe(III) and Mn(IV) minerals. It seems that the oxidation of reduced Fe and Mn in the river is much slower and should be modeled as a kinetic process. The error for Ba is also large. Limited equilibration of the river water with the atmosphere is also supported by high calculated $\log P_{CO_2}$ values (Table 3) and relatively low pH values (Table 2).

Table 4 Results of direct geochemical modeling of water chemistry evolution in the Bierawka River (see text for modeling scenarios)

Parameter/scenario	pH	Ca	Mg	Na	HCO ₃	SO ₄	Cl	Fe	Mn	Ba	Sr	NH ₄	NO ₃
PP12-reactions	7.25	144	132	2647	294	669	6095	<0.1	<0.1	0.025	3.16	0	11.7
Δ [%]	+4.9	+11.9	+7.3	+4.5	-13.9	-16.4	-2.5	n.d.	n.d.	-248	+10.5	n.d.	+172
PP12-only mixing	7.48	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	2.72	0.56	0.105	n.c.	2.19	0
Δ (%)	+4.6	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	+128	+39.6	+20.7	n.c.	>1000	n.d.

n.d. not determined due to very low or zero calculated concentration, *n.c.* no change compared to reaction case

The third row shows results of conservative mixing, e.g., no geochemical reactions are included in scenario (b). The differences between the calculated and measured values are seen in the fourth row. For species like Na, Cl, and SO_4 , the results are the same. The principal differences are in Fe, Mn, and Ba. The error for Fe is still large, but the agreement for Mn and Ba is much better. This supports the hypothesis about slow equilibration of the river water with atmosphere. Nitrogen species represent a special case. In scenario (a), all of the ammonia is oxidized to nitrate, which is not a realistic situation. In scenario (b), the calculated ammonia is overestimated, and there is no nitrate.

High concentrations of Na, Cl, and SO_4 in the Bierawka River represent highly undesirable conditions because the confluence of the Bierawka River with the Odra River is only about 40 km west of the Smolnica site. These concentrations are higher than those permitted by Polish law for surface waters, which is 1,000 mg/l for Cl and 500 mg/l for SO_4 (Ministry of Environment 2002). Water in the Odra River is already contaminated from several mining sites above the confluence with the Bierawka River. However, the contribution of small streams like the Bierawka River may further limit the use of its water for recreation and other purposes.

Conclusions

Contamination by sulfate, Cl, Na, NH_4 , and Fe has been found in the aquifer between the coal waste pile and the Bierawka River at the Smolnica site. Contamination results from the oxidation of pyrite and flushing of residual brine. Values of pH are generally slightly acidic or neutral (6.0–7.0) as a consequence of neutralization of acidity produced by the oxidation of pyrite by dissolution of carbonates. This pH range also favors precipitation of Fe(III) hydroxides on the surface of pyrite, thus lowering the dissolved iron concentrations. High concentrations of sulfate suppress Ba concentrations by the precipitation of barite, with resulting lower Ba concentrations in the upgradient background groundwater. Dissolution of carbonates is indicated by elevated Sr concentrations because Sr is present in carbonates as an accessory

species. Species like Na, Cl, and NH_4 originate in brine, which was initially present in the waste material and is gradually flushed out.

Based on speciation modeling, the behavior of sulfate in the aquifer between the pile and the Bierawka River is conservative, i.e. there is no precipitation of secondary sulfate minerals. Furthermore, the redox potential is too high for sulfate reduction [the Eh is between the nitrate reduction level and Fe(III) reduction level]. However, precipitation of gypsum directly in the pile is probable. Some groundwater samples are supersaturated with respect to Fe(III) minerals such as amorphous $\text{Fe}(\text{OH})_3(\text{a})$, suggesting precipitation of this phase. Dissolved Mn concentrations in samples with high alkalinity are probably controlled by the precipitation of rhodochrosite, MnCO_3 . Concentration of Ba seems to be controlled by the precipitation of barite. The behavior of Sr seems to be conservative.

There is a statistically significant declining trend of Cl concentrations in the most highly contaminated well P4. However, no such trend is observed for Na, which was initially present in the brine because Na flushing is retarded by its release from cation exchange sites. At P4, there are also statistically significant increasing trends for Mg and pH. The molar ratio Ca/Mg decreases in time, suggesting that less soluble dolomite becomes more important over time in pH neutralization. At site P2, the trends are much less pronounced. The principal difference between both sites is in an almost constant and high molar Ca/Mg ratio at the P2 site.

Hydraulic head profiles in the river bottom sediments indicate an upward flux toward the river, but there are significant differences between the sites. The flux at the more sandy MP2 site close to P2 is double compared to the flux at the MP4 site, which has a higher clay content. The pore water sampled in the river sediments indicates that most species including sulfate are transported conservatively into the river. In contrast, there seems to be precipitation of Fe oxide and hydroxides and Mn-carbonate rhodochrosite, MnCO_3 , at the groundwater /river water interface.

Water in the Bierawka River is already strongly contaminated by sodium, chloride, and sulfate upgradient from the Smolnica pile. The input of

groundwater contaminated from the pile results in about a 30% increase in sulfate concentrations in the river but with some dilution and attenuation of sodium and chloride. There is only a slight increase of Fe and Mn downgradient from the pile and concentrations of Sr, Ba, and NH₄ decrease.

Direct geochemical modeling results suggest that there is not fast equilibration with atmospheric CO₂ and O₂, and thus, carbonate and redox reactions should be treated as kinetic reactions. Sodium, chloride, and sulfate behave conservatively in the river water. A relatively large difference between the measured and modeled sulfate concentrations was found (about 16.4%); however, an excellent agreement was found between measured and modeled concentrations for chloride (error about 2.5%). The error for sulfate was probably caused by hidden sulfate input to the river between the groundwater monitoring wells.

High concentrations of Na, Cl, and SO₄ in the Bierawka River represent an additional contamination source for water in the Odra River, which is joined by the Bierawka River farther downgradient. Water in the Odra River is already contaminated from several mining sites above the confluence with the Bierawka River, which limits the use of the water for recreation and other purposes.

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