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Selected ions and major and trace elements as contaminants in coal-waste dump water from the Lower and Upper Silesian Coal Basins (Poland)

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Abstract Many temporary and permanent reservoirs of water occur on or near coal-waste dumps in the Lower- and Upper Silesian Coal Basins (Poland). Little or nothing is known of the degree to which their water chemistry might reflect (i) reservoir type, i.e., whether permanent or temporary, (ii) level of coal-waste thermal activity, i.e., whether inactive or self-heating or burnt-out or (iii) region, i.e., whether the dumps are in Upper- or Lower Silesia. To provide some answers, concentrations of selected ions (NH_4^+ , HCO_3^- , F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) were determined by ion chromatography and of nineteen elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, Pb, S, Si, Sr, Zn) by inductively coupled plasma mass spectrometry (ICP-MS). The data allow a number of the following observations. When permanent reservoirs are considered, there is a clear relationship between concentrations of ions and major and trace elements and dump thermal activity. The highest concentrations occur where the thermal activity is high as inorganic components are transformed into more water-soluble forms. As dump thermal activity shows a regional pattern, it follows also that elemental and ion concentrations in the dump waters show significant regional differences. In temporary reservoirs, concentrations of ions and major and trace elements are much lower and any correlations between components less significant than in the permanent reservoirs; these reservoirs exist for too short a time for any balance between coal waste- and water components to be established.

Keywords Coal-waste dump water · Self-heating · Main ion concentrations · Major elements · Trace elements

1 Introduction

1.1 Coal waste and coal-waste dump waters

The coal industry everywhere generates large amounts of waste rock mainly stored in dumps and landfills. Only a small proportion of this material is suitable for road building or other purposes as most is not inert (Younger 2004; Sokol et al. 2005; Kłojzy-Karczmarczyk et al. 2016; Klatka et al. 2017). Although there has been growing concern about the environmental impact of long-term storage of this waste in recent years (e.g., Finkelmann 2004; Pone et al. 2007; Ribeiro et al. 2010; Misz-Kennan and Fabiańska 2011), their impact on the water environment has been mostly neglected.

The Upper- and Lower Silesian Coal Basins (USCB and LSCB), Poland, are two large coal basins where bituminous

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coal has been mined since the 1800s. In these, mudstones, claystones and coaly shales dominate in coal waste. Coal-waste minerals mainly include clay minerals (50%–70%), quartz (20%–30%) and other minerals (10%–20%), e.g., chlorite, pyrite, siderite, ankerite, gypsum and jarosite (Skarżyńska 1995; Kruszewski 2019a, b). Elements occur in the inorganic matrix as main- or trace components of minerals or as adsorbed elements in the inorganic fraction while, in the organic fraction, they occur as organometallic-, chelate- or ion-exchange compounds (Baruah et al. 2003). Due to the sorption capacity of clay minerals, waste rock can host a variety of trace elements, including rare earth elements (Finkelman 2004; Ribeiro et al. 2010; Zhou et al. 2012; Nowak 2013; Ciesielczuk et al. 2014; Yang et al. 2016; Nowak and Kokowska-Pawłowska 2017; Guo 2018). During weathering, these can be transferred to soil and water. Oxidative weathering of iron sulphides, e.g., pyrite and marcasite, may release trace metals into water (Huggins et al. 2011; Kolker 2012). However, as Na and Ca mineral dissolution may give rise to insoluble sulfate minerals, e.g., jarosite and gypsum, that act as a buffer maintaining leachate pH close to neutral, mobilization of iron and trace metals is minimized (Huggins et al. 2011).

There are numerous descriptions from coal basins worldwide of the behaviour during combustion of main- and trace elements in coal (e.g., Swaine 1990; Querol et al. 1995; Pusz et al. 1997; Baruah et al. 2003; Xu et al. 2003; Yudovich and Ketris 2002, 2015; Lewińska-Preis et al. 2009; Dai et al. 2012, 2014, 2017; Kolker 2012; Hower et al. 2016). Due to much higher mineral contents, the mobility of trace elements in coal waste is expected to differ significantly from that in coal (Li et al. 2011; Zhou et al. 2014; Pierwoła et al. 2018). However, there are relatively limited data about the behaviour of elements in coal waste during self-heating; some exceptions are Guo (2018), Kruszewski (2019a, b), Nowak et al. (2017), Sokol et al. (2005), and Zhao et al. (2008). There has been some indication that contents of Zn, Cu, Cd, Pb, and Ni in coal-waste dumps in Poland exceed average contents in Polish soils; average values in range from 26.6 to 170.0 mg/kg for Pb, 40.3–709.2 mg/kg for Zn and 23.5–56.25 mg/kg for Cu (Szopka et al. 2010; Kłojzy-Karczmarczyk et al. 2016; Klatka et al. 2017). According to the Regulation of the Minister of the Environment (2011) on the criteria for classifying extractive waste, coal-waste material is not inert as S, Zn, Pb, and Cd, Cr, Ni, Co and V contents are too high (Kłojzy-Karczmarczyk et al. 2016). The coal waste pH is slightly alkaline, from 7.26 to 9.24 (Bojarska and Bzowski 2012; Klatka et al. 2017).

Even less is known about the migration of these elements into soil and surface waters. Some leaching tests (e.g., Huggins et al. 2011; Pierwoła et al. 2018; Yang et al. 2016 and Zhang et al. 2015) and research on gangue

environmental impact (Li et al. 2011) indicate that many factors such as pH, type of mineral matrix, mode of element occurrence (water-leachable, ion-exchangeable, organic-bound, carbonate-bound, silicate-bound, sulfide-bound), associated elements or method of leaching can affect element mobility (Guo 2018).

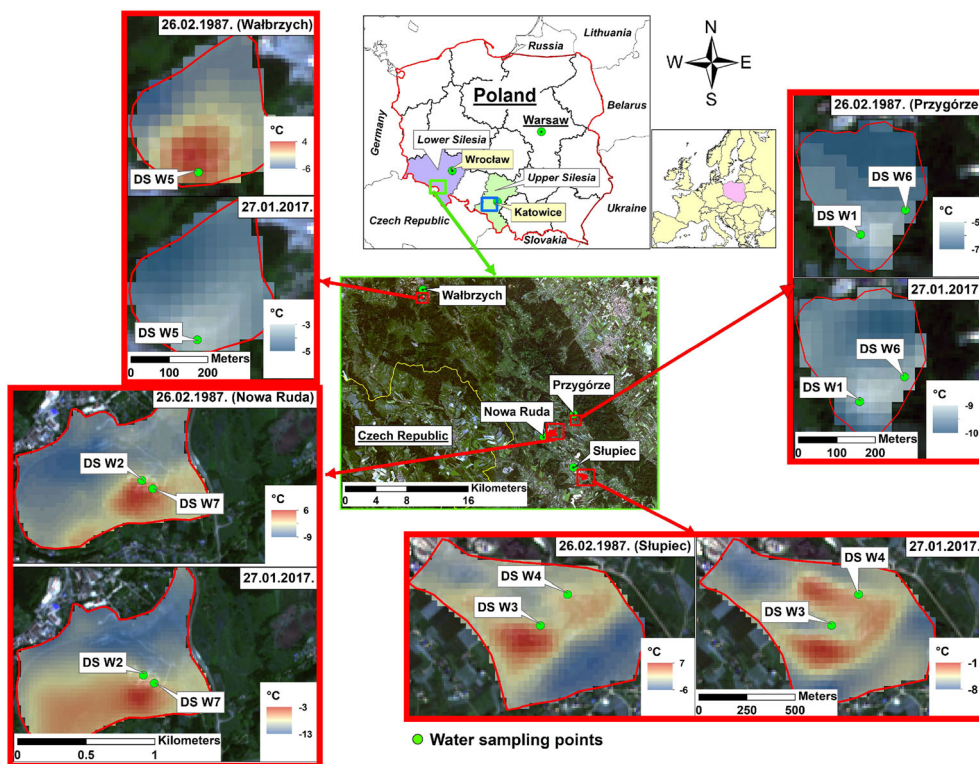
In Poland, there are two basic legal acts regarding water (Kamińska and Strzemieczna, 2018). The Act of 7 June 2001 (Journal of Laws 2018, item 1152) regulates collective water supply and wastewater disposal and the Regulation of the Minister of Health (Journal of Laws 2017, item 2294) water quality for human consumption. Acceptable standards for drinking water are specified for a variety of microbiological- and chemical parameters and radioactive-element content, etc. Separate regulations cover waters not meeting these standards that are released into circulation. Leachate waters discharged from dumps, waste disposal facilities and waste storage places must not contain substances harmful to the aquatic environment in amounts exceeding the maximum permissible values of pollution indicators for industrial wastewater specified by the Minister of Maritime Economy and Inland Navigation (Journal of Law 2019, item 1311; Table S1 in Supplement Material).

In this regulatory context, it is important to establish the composition of natural coal-waste leachates and whether any migration out of coal-waste dumps poses a hazard to the aquatic environment and groundwater. Rainwater easily penetrates porous dumps, dissolves waste components and acts as a transporting agent (e.g., Li et al. 2011). In this work, we aim to assess what ions and major- and trace elements are leached, and in what concentrations, to various water reservoirs located on selected coal-waste dumps and in their vicinities. Comparisons between the USCB and LSCB and types of water reservoirs are drawn to help determine the factors influencing waste-dump water compositions. The significance of self-heating in driving element mobility is given some emphasis.

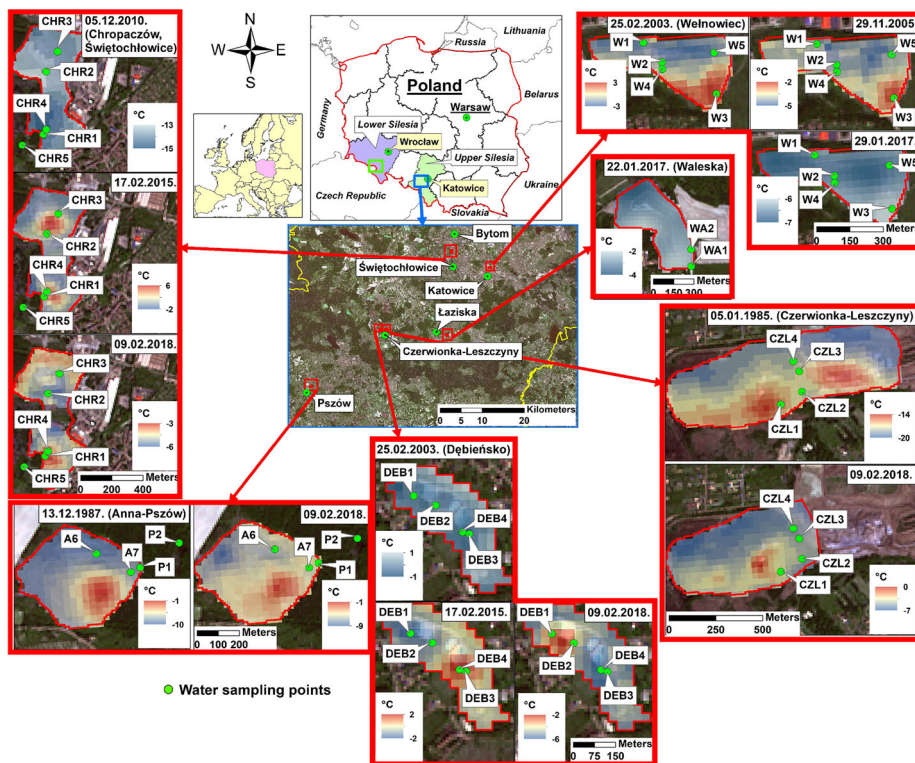
1.2 Geological setting

1.2.1 Lower Silesia Coal Basin (LSCB)

In the Pennsylvanian LSCB in southwestern Poland (Fig. 1a), economic bituminous coal seams covering an area of ~ 350 km² belong to the Wałbrzych and Żacleń Formations, and part of the Glink Formation. The quality of the coals varies considerably; Ro values range from 0.72%–5.03% in the Wałbrzych area and from 1.13% to 1.59% in the Nowa Ruda area (Bossowski, 1995). Maceral composition is typically vitrinite dominant although the coals are often inertinite-rich (< 40%; Kotarba and Rice 2001).



(a)



(b)

Fig. 1 Locations of the coal-waste dumps and their thermal maps from images taken at two or three different times to show heating development. **a** LSCB, **b** USCB. Blue and green rectangles show the research areas

In the 1800–1900s, many coal mines now closed operated in the region (Frużyński, 2012). The coal-waste dumps built then lacked fire prevention measures. Over the years, numerous self-heating episodes occurred, some lasting up to now. Attempts to put out the fires mostly failed. Some totally burned-out waste rocks are reddish- and orange-pale yellow, other thermally altered rocks are black-gray, pyrolyzed and rich in bitumen, and some are only slightly oxidized (Fabiańska et al. 2016).

1.2.2 Upper Silesia Coal Basin (USCB)

The USCB covers an area of 7400 km², of which 5800 km² are within Poland and the remainder in the Czech Republic (Fig. 1b). It is the largest of the Polish coal basins with numerous bituminous Pennsylvanian coal seams of varying thickness (0.4–24.0 m), some of which are economic (Jureczka and Kotas 1995; Jureczka et al. 2005). The coals are of varying quality, from poorly coalified power coals to coking coals and anthracites. Vitrinite macerals dominate but ever present liptinite- and inertinite macerals can comprise < 55% (Jureczka and Kotas 1995; Jureczka et al. 2005).

The USCB coal mining started in the 1600s and peaked in the 1970–1980s. There are ~ 200 coal-waste dumps in the region (Sikorska-Maykowska 2001; Skarżyńska 1995). Self-heating occurs in them due, mostly, to outdated methods of coal-waste storage such as deposition of uncompacted material in conical dumps on sites not sealed from below. The rebuilding of some and dismantling of others partially improved matters. Nevertheless, self-heating episodes have transformed the coal waste and promoted the emission of organic- and inorganic substances into the air and soils (Misz-Kennan and Fabiańska 2011; Fabiańska et al. 2013; Misz-Kennan et al. 2013; Ciesielczuk et al. 2014; Nádudvari et al. 2018).

1.3 Mapping of thermal activity within coal-waste dumps

Generally, coal-waste self-heating hot spots can be detected on satellite images where the fire is intense. These spots have surface temperatures between 4 and 14 °C higher than background surface temperatures (Fig. 1). As the resolution of the thermal bands of the applied Landsat series varies from 60–120 m, hot spots related to fires falling below such resolutions, or with low surface temperatures, cannot be detected.

1.3.1 Thermal activity in LSCB dumps

Remote sensing enables self-heating of variable intensity occurring in the dumps to be investigated. In the

Wałbrzych dump, a hot spot associated with intense fire within the dump in 1987 is waning now. The Przygórze dump shows no evidence of intense heating. Thermal activity is ongoing in the Słupiec- and Nowa Ruda dumps. Since 1987, a new hot spot has appeared in the northern part of the Słupiec dump and a similar hot spot has been detected in Nowa Ruda despite subzero background temperatures (Fig. 1a).

1.3.2 Thermal activity in USCB dumps—the Katowice Region (USCB-K)

In the Chropaczów dump, intensive thermal activity started in 2014–2015 after its exploitation for building materials began (Kita 2015). Two large active hot spots developed (Fig. 1b). It is possible, however, that the dump was in a state of low thermal activity before its opening. It is difficult to distinguish thermal processes on satellite images of the Wełnowiec dump. An area of intense self-heating on the inclined slope is relatively small. However, in 2003, a small self-heating spot appeared on the eastern side of the dump. On the northern side, hot spots fall below the satellite sensitivity limits. A hot spot at the top of the highest cone in the Czerwionka-Leszczyny dump has been waning since the early 1985s (Nádudvari 2014; Nádudvari and Ciesielczuk 2018). Self-heating has also occurred on the eastern side (Fig. 1b). Burned-out waste there is now being excavated and used for highway construction, etc. (Nádudvari and Ciesielczuk 2018).

1.3.3 Upper Silesia dumps—the Rybnik Region (USCB-R)

The Anna dump showed intense heating activity in 2001, 2004 and 2010, despite ambient temperatures < 0 °C; the increased activity was a response to exploitation (Fabiańska et al. 2018; Nádudvari 2014). Today, activity is waning though the size of the visible spot is stable (Fig. 1b). Several hot spots were detected on the Dębieńsko dump in 2015 and 2018 (Fig. 1b); measured temperature ranges indicate relatively mild self-heating with small hot spots. However, residential houses are sited close to these spots (<http://www.nowiny.rybnik.pl/artykul,40981,halda-plonie-od-miesiacy.html>). The Waleska dump shows no evidence of heating.

2 Experimental

2.1 Sampling

The subject of the research was water from reservoirs occurring on or in the immediate vicinity of coal-waste dumps from the LSCB and two areas of the USCB, namely,

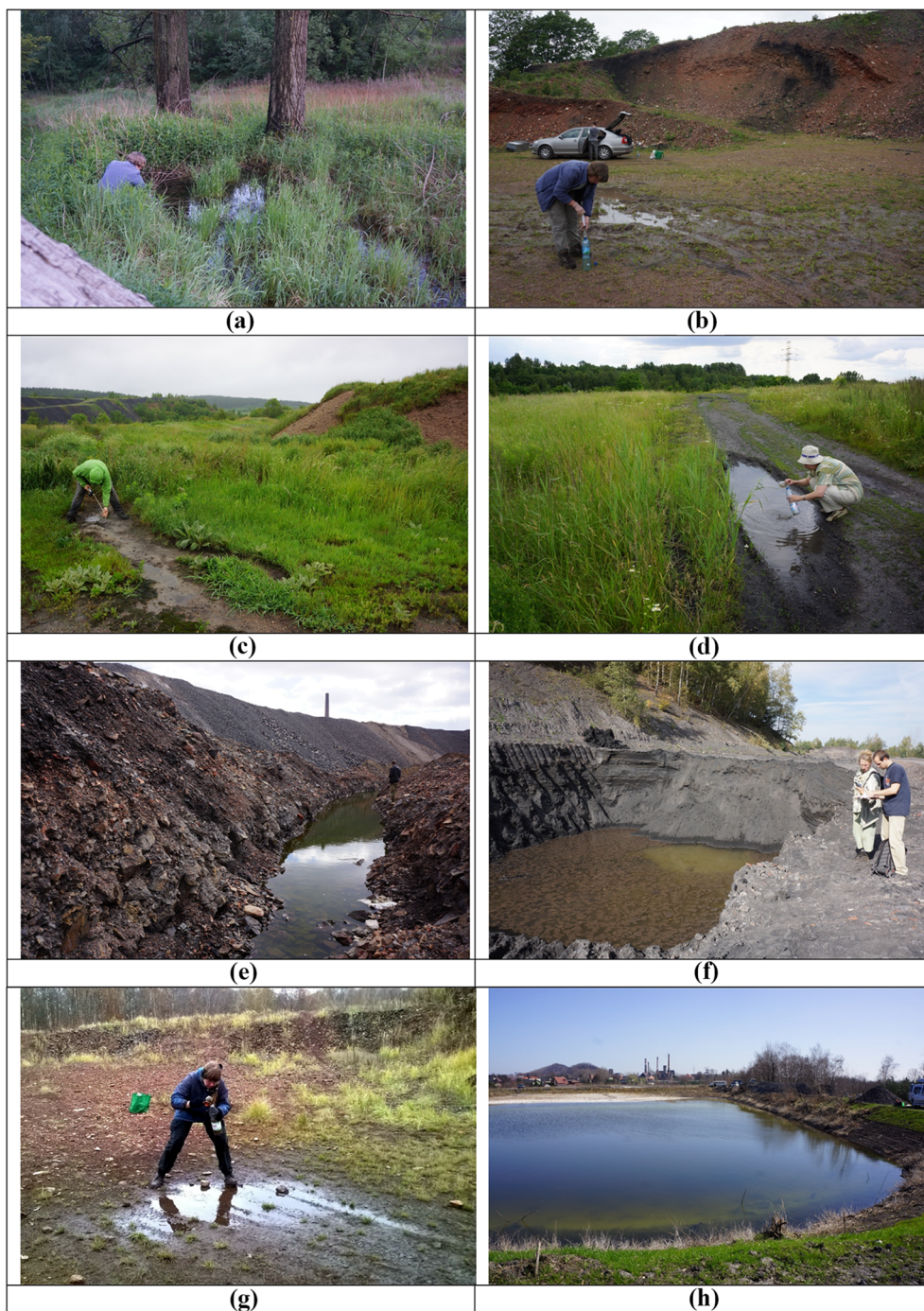


Fig. 2 Sampling points: **a** Lake at the foot of Wałbrzych dump (sample DS-W4); **b** puddle at the foot of Przygórze dump (sample DS-W5); **c** hollow at the vent outlet at the Słupiec dump (sample DS-W7); **d** puddle at the foot of Welnowiec dump (sample W2); **e** pond at the Chropaczów dump (sample CHR3); **f** settler (pond) at the foot of Czerwionka-Leszczyny dump (sample CZL3); **g** puddle at the Anna-Pszów dump (sample A7); **h** settler (pond) with saline water at the Dębieńsko dump (sample DEB1). Phot.: J. Ciesielczuk & M. Misz-Kennan

the Rybnik (USCB-R) and the Katowice (USCB-K) regions. The LSCB self-heating dumps are in the towns of Słupiec and Nowa Ruda. Excepting the Waleska dump, all the USCB dumps investigated were self-heating at the time of sampling. In total, 31 samples of water (ca 1500 mL) were collected from lakes, puddles, settlers (ponds), and

streams. Sampling points are shown on Fig. 2 and described in Table 1. The samples were collected and stored in accordance with PN—ISO5667-5: 2017–10. Before analyses, the samples were filtrated on Millipore mixed cellulose ester filters $\Phi 47$ mm, $0.45 \mu\text{m}$ pore size. The total water volume prepared for analysis was 1000 cm^3 . After

Table 1 List of dump water samples, description of sampling sites and type of water reservoir

No.	Sample code	Coal-waste dump	Type of water reservoir	Description of sampling sites, reservoir parameters
<i>Lower Silesia Coal Basin (LSCB)</i>				
1	DS-W1	Przygórze	Permanent	A lake at the dump foot, with visible life signs (water plants), 6 m in diameter, 1–2 m deep
2	DS-W2	Nowa Ruda	Temporary	A puddle ca 15 m below the dump peak, located on coal wastes, 7 m in diameter, 0.4 m deep
3	DS-W3	Słupiec	Permanent	A lake overgrown with canes, 25 m in diameter, 2 m deep
4	DS-W4	Wałbrzych	Permanent	A lake at the dump foot, 10 m from the dump, 8 m in diameter, 1–2 m deep
5	DS-W5	Przygórze	Temporary	A puddle at the dump foot, 3 m in diameter, 0.3 m deep
6	DS-W6	Nowa Ruda	Temporary	A puddle at the dump top, 1 m in diameter, 0.1 m deep
7	DS-W7	Słupiec	Temporary	A hollow at the vent outlet 0.1 m in diameter, 0.05 m deep
<i>Upper Silesia Coal Basin, the Katowice Region (USCB-K)</i>				
8	W1	Wełnowiec	Temporary	A puddle at the dump foot, 5 m in diameter
9	W2	Wełnowiec	Temporary	A puddle at the dump top, 1 m × 5 m, 0.2 m deep
10	W3	Wełnowiec	Temporary	A puddle at the dump foot, 1 m × 5 m, 0.05 m deep
11	W4	Wełnowiec	Temporary	A puddle at the dump top, 1 m × 3 m
12	W5	Wełnowiec	Temporary	A puddle at the dump top, 4 m in diameter
13	CHR1	Chropaczów	Temporary	A puddle at the dump top, 5 m in diameter
14	CHR2	Chropaczów	Temporary	A puddle at the dump top, 8 m × 20 m, 0.5 m deep
15	CHR3	Chropaczów	Permanent	A lake, 50 m long, 3 m wide, 0.5 m deep
16	CHR4	Chropaczów	Temporary	A puddle at the dump top, 2 m × 2 m, 0.1 m deep
17	CHR5	Chropaczów	Permanent	A lake, close to the dump and smelter wastes, 30 m × 200 m, 10 m deep
<i>Upper Silesia Coal Basin, the Rybnik Region (USCB-R)</i>				
18	CZL1	Czerwionka-Leszczyny	Temporary	A puddle on coal wastes in a forest, 2 m × 3 m, 0.8 m deep
19	CZL2	Czerwionka-Leszczyny	Permanent	A settler at the dump foot, 10 m × 8 m, 1.5 m deep
20	CZL3	Czerwionka-Leszczyny	Permanent	A settler at the dump foot, 15 m × 10 m, 2 m deep
21	CZL4	Czerwionka-Leszczyny	Permanent	A settler at the dump foot, 12 m × 8 m, 2 m deep
22	P1	Anna-Pszów	Permanent	A stream flowing from under the dump with life signs visible (plants, water insects), water sampled at the dump margin
23	P2	Anna-Pszów	Permanent	A lake accumulating water from the stream (above) in its lower course,
24	A6	Anna-Pszów	Temporary	A puddle, 2 m × 5 m, 0.08 m deep
25	A7	Anna-Pszów	Temporary	A puddle, 1 m × 2 m, 0.05 m deep
26	DEB1	Dębieńsko	Permanent	A settler with saline water, the closest to the excavation in the dump made during fire-fighting action, 10 m × 10 m, 1.5 m deep
27	DEB2	Dębieńsko	Permanent	A settler with saline water, the second from the excavation in the dump made during fire-fighting action, 12 m × 10 m, 2 m deep
28	DEB3	Dębieńsko	Permanent	A settler with saline water, the third from the excavation in the dump made during fire-fighting action, 10 m × 10 m, 1.5 m deep
29	DEB4	Dębieńsko	Permanent	Water sampled from the pipe collecting water from under the dump and the settlers
30	WA1	Waleska	Permanent	A stream flowing along the dump margin
31	WA2	Waleska	Permanent	A settler at the dump top

pH and conductivity measurements but prior to other analyses, all samples were acidified to prevent precipitation. Each sample was divided into two parts, one for ion chromatography, the other by ICP-MS analyses.

2.2 pH and conductivity

Water pH was measured on an Elmetron CP-315 pH-meter with temperature compensation equipped with a glass-

Table 2 Occurrence of trace elements and ions in coal-waste dump waters in Silesian coal basins

Element	Arithmetic average	Coefficient of variation	Arithmetic average	Coefficient of variation	Arithmetic average	Coefficient of variation
	Lower Silesia Coal Basin (LSCB)	Lower Silesia Coal Basin (LSCB)	Upper Silesia Coal Basin, the Katowice region (USCB-K)	Upper Silesia Coal Basin, the Katowice region (USCB-K)	Upper Silesia Coal Basin, the Rybnik region (USCB-R)	Upper Silesia Coal Basin, the Rybnik region (USCB-R)
	X_{ar} (ppb)	V_x (%)	X_{ar} (ppb)	V_x (%)	X_{ar} (ppb)	V_x (%)
Al	174.89	76.08	100.25	104.06	5.65	147.71
B	112.56	95.51	366.4	75.31	1991.57	121.20
Ba	55	60.15	42.6	71.74	275.5	155.80
Cd	0.49	–	0.49	–	0.49	–
Cr	2.80	–	2.8	–	2.8	–
Cu	4.11	20.21	23.06	183.54	5.54	87.41
Fe	17.31	114.22	8.77	233.29	2.97	87.49
Li	18.71	32.75	88.2	146.28	4106.07	218.13
Mn	8.14	102.12	35.4	138.77	964.79	170.04
P	148.83	146.16	76.2	124.3	122.94	203.47
Pb	90.3	–	90.3	–	90.3	–
Sr	142.71	95.76	655.2	81.71	8513	168.32
Zn	41.16	82	105.45	117.84	86.14	40.78
NH ₄ ⁺	34.29	171.61	506	131.01	24,552.14	156.99
F ⁻	474.43	66.08	462.7	102.41	19,445.71	143.54
NO ₃ ⁻	166.71	96.46	672	44.45	12,715.71	141.64
PO ₄ ³⁻	4.29	172.89	659	195.62	–	–
	X_{ar} (ppm)	V_x (%)	X_{ar} (ppm)	V_x (%)	X_{ar} (ppm)	V_x (%)
Ca	45.72	89.96	106.5	34.79	257.79	82.76
K	6.01	70.2	20.2	61.91	234.86	170.49
Mg	13.57	107.36	51.6	106.61	270.29	78.60
Na	4.02	136.55	119.6	107.19	1034.86	110.73
S	62.29	121.92	709.4	61.37	2493.43	134.35
Si	2.96	84.87	2.53	111.37	2.36	152.94
HCO ₃ ⁻	140.29	76.21	175.86	86.36	208.29	84.61
Cl ⁻	6.35	130.66	242.95	175.85	21,925.36	183.58
Br ⁻	0.05	125.63	1.05	163.98	78.19	195.86
NO ₃ ⁻	1.81	153.63	25.15	214.05	82.44	150.15
SO ₄ ²⁻	63.57	121.47	274.87	125.9	3222.93	130.07

combined electrode. Water conductivity was measured with a CC-401 conductometer with temperature compensation.

2.3 Ion chromatography

Nine ions present in high concentrations, NH₄⁺, HCO₃⁻, F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, were determined by ion chromatography. An 850 Professional IC (prod. Metrohm) ion chromatograph with a Supp 7–250/4.0 column for anion analysis and Metrosep C-4–150/4.0 for cations was used. An eluent of 3.6 mmol/L NA₂CO₃

($f = 0.7$ mL/min) was used for anions and one of 1.7 mmol/L HNO₃ and 0.7 mmol/L of dipicolinic acid ($f = 0.9$ mL/min) for cations. The limits of detection (mg/L) were 0.01 for Ca²⁺ and Mg²⁺, 0.02 for Na⁺ and NH₄⁺, 0.03 for K⁺, 0.02 for F⁻, NO₂⁻, Cl⁻, and Br⁻ and 0.01 mg/L for NO₃⁻ and SO₄²⁻.

2.4 ICP-MS

Nineteen elements, i.e., Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, Pb, S, Si, Sr, and Zn were quantitatively determined by inductively coupled plasma—mass

Table 3 Occurrence of trace elements and ions in coal-waste dump waters in Silesian coal basins: Statistics

Element	Coefficient of variation		Coefficient of variation	
	Arithmetic average	Permanent water reservoirs	Arithmetic average	Temporary water reservoirs
	X_{ar} (ppb)	V_x (%)	X_{ar} (ppb)	V_x (%)
Al	30.42	225.89	121.27	101.92
B	1799.99	128.5	235.6	83.11
Ba	221.44	184.56	75	132.22
Cd	0.49	–	0.49	–
Cr	2.8	–	2.8	–
Cu	5.33	85.44	16.79	209.44
Fe	5.14	222.49	11.22	167.13
Li	3628.06	232.63	29.93	92.33
Mn	723.38	212.29	156.27	339.52
P	110.74	212.45	116.88	139.38
Pb	90.3	–	90.3	–
Sr	7485.25	182.14	464.6	103.38
Zn	103.69	93.17	59.31	69.86
NH ₄ ⁺	21,035.63	176.14	830.67	283.46
F ⁻	17,080.63	156.76	459.87	93.1
NO ₃ ⁻	11,287.69	152.49	353.6	93.72
PO ₄ ³⁻	1.06	400	440.2	245.83
	X_{ar} (ppm)	V_x (%)	X_{ar} (ppm)	V_x (%)
Ca	236	88.3	81.2	58.12
K	208.07	182.61	13.53	72.71
Mg	253.75	80.47	22.33	63.13
Na	931.88	118.61	53.47	151.61
S	2332.75	135.31	340.93	94.53
Si	3.12	118.37	1.94	110.84
HCO ₃ ⁻	265.94	63.19	93.44	62.75
Cl ⁻	19,274.32	198.01	69.32	255.14
Br ⁻	68.81	210.55	0.31	161.39
NO ₃ ⁻	84.48	140.5	4.45	194.38
SO ₄ ²⁻	2842	142.11	189.51	160.87

spectrometry (ICP-MS) using an ICP JI 50p spectrometer. Conditions of the analysis, analytical lines and integration times are given in Supplement. All elements were determined with the monochromator except for Li for which the polychromator was used. In preparing the calibration curves, five standards were used. The raw results are shown in Table S2 in Supplement Material and their statistics in Tables 3S–7S.

2.5 Statistical analysis

All calculations were performed using the StatSoft STATISTICA and PQStat software (test version). In the initial stage of the analysis, the basic statistical characteristics

were calculated (measures of location and dispersion) which enabled the data to be summarized and basic conclusions and generalizations drawn. To determine the average level and distribution of element- and ion concentrations, the arithmetic means (X_{ar}) and quartiles $Q_1 = 25\%$, $Q_2 = \text{median} = 50\%$, $Q_3 = 75\%$ were calculated. To determine the variation area of element- and ion concentrations, the range ($R = \text{max} - \text{min}$), the standard deviation (S_x), and the coefficient of variation (V_x) were calculated. To illustrate the basic numerical characteristics (concentrations of elements and ions) box-whisker plots were made showing the minimum (X_{\min})- and maximum (X_{\max}) concentrations of a given element or ion and the differentiation between typical units (interquartile range, $IQR = Q_3 - Q_1$). The differentiation of the variable values (value of the element- and ion concentrations) was evaluated by comparing the length of four sections $< X_{\min} - Q_1 >$, $< Q_1 - \text{Me} >$, $< \text{Me} - Q_3 >$, $< Q_3 - X_{\max} >$.

The normality of the distribution was tested using the Kolmogorov–Smirnov-, Lilliefors- and Shapiro–Wilk tests. Spearman's rank-order correlation coefficient was calculated to investigate the relationship between the concentrations of elements and ions in the permanent- and temporary reservoirs and the regions of the LSCB and USCB.

To group reservoirs showing similar element- and ion concentrations, cluster analysis was performed. Initially, each object was treated as a separate cluster. The nearest reservoirs were then gradually merged into new clusters until one cluster was acquired (agglomeration method). The dendrograms were created using the Euclidean distance and Ward's method (Stanisz 2006a, b).

3 Results

3.1 Inorganic geochemistry of coal-waste dump water

The ICP-MS results are considered below in terms of:

- (1) Average concentrations of leached elements and ions and variability of their occurrence in the waters infiltrating the coal-waste dumps.
- (2) Differences in the concentrations of the elements investigated in waters originating from currently inactive self-heated coal-waste dumps, thermally active dumps and dumps that never ignited.
- (3) Differences in element- and ion concentrations in permanent- and temporary reservoirs.
- (4) Regional trends and correlations between the LSCB and the USCB (Rybnik- and Katowice regions).

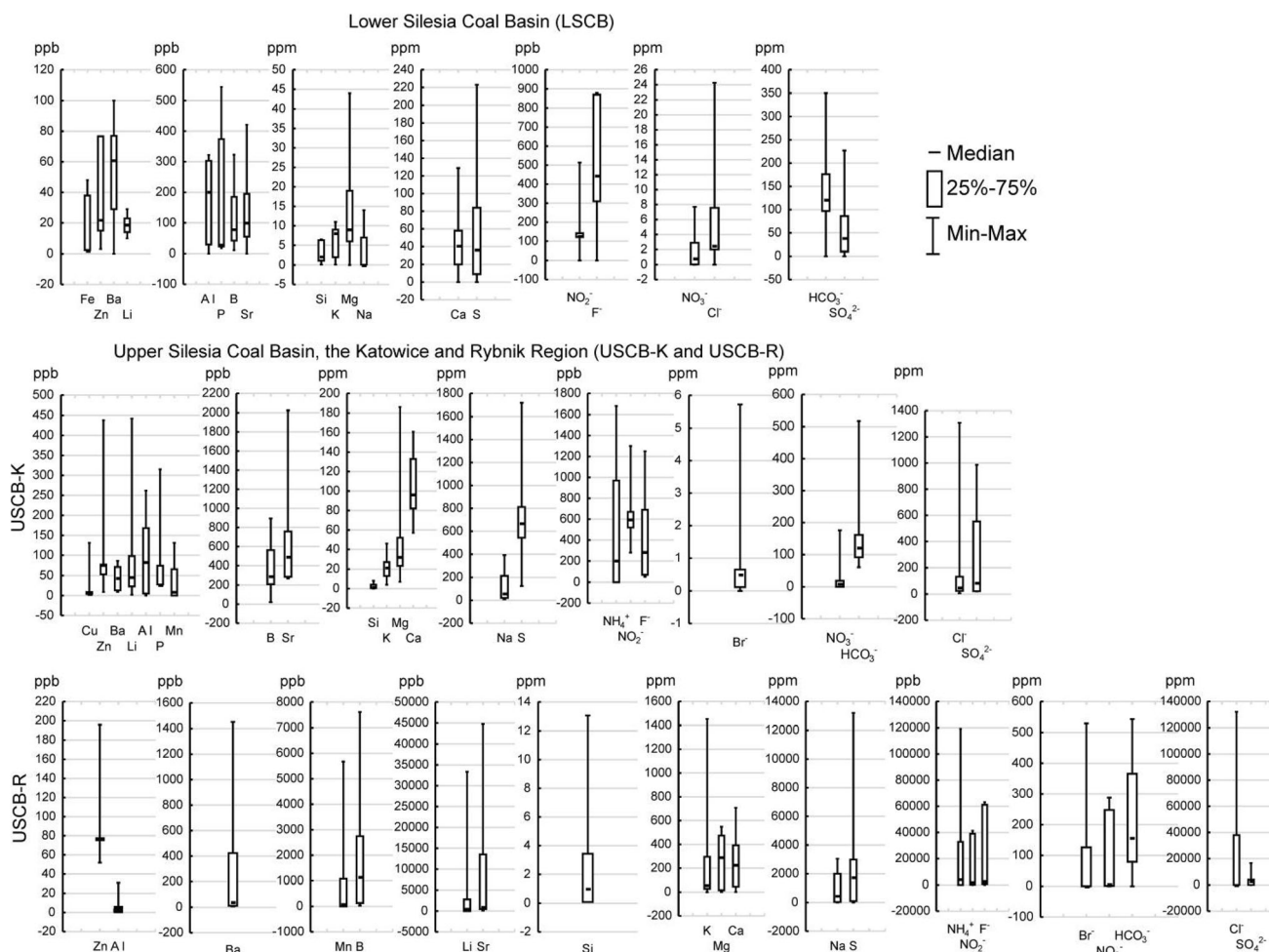


Fig. 3 Box-whisker plots of ion- and trace-element concentrations for LSCB and USCB

(5) Correlations between concentrations of ions and major- and trace elements.

Statistics characterizing the concentrations (arithmetic mean X_{ar}) and variability of element occurrence (variation coefficient V_x) in the dump waters are given in Tables 2 and 3.

Of the sample population, 52% came from small but permanent water reservoirs (ponds) located at the dumps foot and 48% from stagnant waters in puddles on the dumps and in their vicinity. In the USCB-R set, 78% of samples come from lakes and, in the USCB-K set, 20%. In the LSCB set, 52% of samples came from puddles and the remainder from ponds.

The elements with the highest concentrations (in ppm) in water are S (62.29–2493.43), Na (4.02–1034.86), Ca (45.72–257.79), Mg (13.57–270.29) and K (6.01–234.86). Cu shows the lowest concentrations (23.06–4.11 ppb). Sr concentrations range from 142.71–8513 ppb and B concentrations range from 112.56 to 1991.57 ppb. The average concentrations of Ba, Mn, and P are 55–275.5 ppb, 8.14–964.79 ppb, 148.83–122.94 ppb, respectively. The

average concentrations of Fe are low and range from 2.97 to 17.31.45 ppb. The average concentrations of Zn range from 41.16 to 105.45 ppb (Table 2). Li concentrations range from 18.71 to 4106.07 ppb. The highest concentrations of major- and trace elements characterize the Rybnik dump waters and the lowest, the LSCB dumps waters. Only Al, Fe, and P show an opposing trend with the highest concentrations in LSCB- and the lowest in USCB waters (Tables 2 and 3).

Among the ions, the highest concentrations are shown by Cl^- (6.35–21,925.36 ppm), SO_4^{2-} (63.57–3222.93 ppm) and HCO_3^- (140.29–208.29 ppm) and the lowest by Br^- (78.19–0.05 ppm) and NH_4^+ (24,552.14–34.29 ppb). As with the major- and trace elements, high ion concentrations occur in waters from the Rybnik dumps. The lowest ion concentrations are in the LSCB waters (Table 2 and Table 3S in Supplementary Material).

The highest average variations of occurrence (> 100%) characterize the following elements in the following places:

LSCBFe, Mg, Mn, Na, P, and S.

USCB-KAl, Cu, Fe, Li, Mg, Mn, Na, P, Si, Sr, and Zn.

USCB- RAl, B, Ba, K, Li, Mn, Na, P, S, Si and Sr.

Permanent reservoirsAl, B, Ba, Fe, K, Li, Mn, Na, P, S, Si, and Sr.

Temporary reservoirsAl, Ba, Cu, Fe, Mn, Na, P, Si, Sr.

The lowest average variation (< 50%) is shown by Cu, Li (LSCB) Ca (USCB-K) and Zn (USCB-R). For the remaining elements, the average value of the variation coefficient ranges from 60%–90%. The highest variability of occurrence characterizes waters from the USCB-R dumps and the smallest, waters from the LSCB dumps (Table 2 and Table 3S in Supplement Material).

Most ions show high degrees (> 100%) of variability. Only HCO_3^{2-} in all waters has a variation coefficient < 100%. Ammonium, NO_2^- , and SO_4^{2-} show the lowest variability in USCB-K waters. For the remaining ions, LSCB waters display the lowest variabilities and USCB-R waters the highest (Table 2 and Table 3S in Supplement Material).

The pH values of all samples range from 6.33 (sample W4) to 9.00 (WA2); most range from 7.14 to 7.38 and are thus very slightly basic (Table 2S in Supplement Material). Conductivity shows greater variation with values ranging from 200–700 $\mu\text{S}/\text{cm}$. Lower values characterize temporary reservoirs (270 $\mu\text{S}/\text{cm}$) and waters from self-heating dumps (298 $\mu\text{S}/\text{cm}$), and maximum values by waters from ponds (590 $\mu\text{S}/\text{cm}$) and burned-out dumps (689 $\mu\text{S}/\text{cm}$).

3.2 Regional variability of trace element- and ion occurrence in coal-waste dump waters

The regional variability of concentrations of ions and major- and trace elements is shown on box and whisker plots (Fig. 3). Cd (≤ 0.00049 ppm), Cr (≤ 0.0028), and Pb (≤ 0.0903) are not included in the plots. Other elements were divided into three groups, i.e., those with the lowest-, intermediate- and highest concentrations (groups 1, 2, and 3). The ions were divided into two groups, i.e., those with lower- and higher concentrations (groups 1 and 2).

3.2.1 Lower Silesia Coal Basin (LSCB)

Group 1, elements with concentrations < 540 ppb, are Cu, Fe, Al, Zn, P, Ba, B, Mn, Li, and Sr. Of these, Al, P, B, and Sr show a large range ($R > 312$ ppb) and the most diversified interquartile (Q_3-Q_1) range (Fig. 3 and Tables 2S, 3S in Supplement Material). Among Si, K, Mg and Na, group 2 elements with concentrations < 45 ppm, Mg has the largest range ($R = 44$ ppm) and the greatest interquartile range ($\text{IQR} = 13$ ppm), and Si the smallest ($R = 6.42$ ppm and $\text{IQR} = 5.17$ ppm). Group 3 elements with concentrations < 225 ppm are Ca and S. Sulphur has a larger range

($R = 222.98$ ppm) and interquartile range ($\text{IQR} = 75$ ppm) than Ca ($R = 128.99$ ppm and $\text{IQR} = 38$ ppm) (Fig. 3 and Tables 2S, 3S in Supplementary Material).

Among PO_4^{3-} , NH_4^+ , NO_2^- , F^- , and Br^- , group 1 ions with concentrations < 880 ppb, F^- displays the largest range ($R = 879$ ppb) and the largest interquartile range ($\text{IQR} = 560$ ppb), and PO_4^{3-} the smallest ($R = 17$ ppb and $\text{IQR} = 13$ ppb). Group 2 ions with higher (< 350 ppm) concentrations include NO_3^- , Cl^- , HCO_3^- , and SO_4^{2-} (Fig. 3 and Tables 2S, 3S in Supplementary Material).

3.2.2 Upper Silesia Coal Basin, Katowice Region (USCB-K)

As in LSCB waters, group 1 elements with concentrations < 2020 ppb, i.e. Cu, Fe, Al, Zn, P, Ba, B, Mn, Li and Sr. B and Sr show the largest range ($R_B = 874$ ppb and $R_{Sr} = 1755$ ppb) and the most diversified interquartile range (Q_3-Q_1 , $\text{IQR}_B = 353$ ppb and $\text{IQR}_{Sr} = 471$ ppb). Group 2 elements with intermediate concentrations (< 46 ppm), i.e., Si and K, show higher concentrations than in LSCB waters. Group 3 elements with the highest concentrations (< 1719 ppm) include Mg, Ca, Na and S. Among these, S shows the greatest diversity in the interquartile range (Q_3-Q_1 , $\text{IQR} = 268$ ppm). As in the LSCB, the element with the highest concentrations is S. Mg and Na show higher concentrations than in the LSCB (Fig. 3 and Tables 2S, 3S in Supplementary Material).

Group 1 ions with lower concentrations (< 1680 ppb) are PO_4^{3-} , NH_4^+ , NO_2^- , F^- , and Br^- (< 5.72 ppm). Group 2 ions are NO_3^- , Cl^- , HCO_3^- , and SO_4^{2-} . Generally, ion concentrations in the waters of the Katowice region are higher than those in the LSCB (Fig. 3 and Tables 2S, 3S in Supplementary Material).

3.2.3 Upper Silesia Coal Basin, the Rybnik Region (USCB-R)

Group 1 elements with concentrations < 853 ppb include Cu, Fe, Al, Zn, and P. Group 2 elements with concentrations < 44,750 ppb concentrations comprise Ba, B, Mn, Li, Sr, and Si (< 13.06 ppm). Concentrations of the last three, i.e., Li, Sr, and Si, are much higher in the USCB-R than in both other regions. Group 3 elements with concentrations < 13,199 ppm include K, Mg, Ca, Na, and S. Sulphur has a large range ($R = 13,193$ ppm) and interquartile range ($\text{IQR} = 2885$ ppm) and shows the highest concentrations (Fig. 3 and Tables 2S, 3S in Supplementary Material).

Ion concentrations are much higher in USCB-R waters than in waters elsewhere. The same applies to trace elements. As in LSCB waters, F^- , NO_3^- , Cl^- and HCO_3^- vary significantly in concentration. Cl^- , HCO_3^- and SO_4^{2-} display the highest concentrations (Fig. 3 and Table 2S, 3S

in Supplementary Material). USCB-R waters do not contain PO_4^{3-} . In LSCB waters, it was present in two samples only (13 and 17 ppb). It is the Welnowiec dump (USCB-K region), a municipal landfill covered with coal waste that is responsible for the relatively high PO_4^{3-} averages for the USCB (Table 2S in the Supplement). Low PO_4^{3-} is related to the generally low (approx. 0.2 wt%, ash basis) concentration of P in coal-waste rocks (Ciesielczuk et al., 2014).

4 Discussion

4.1 Origin of inorganic constituents of coal-waste dump water

Coal waste stored in dumps contains a significant proportion (ca 3%–30%) of organic matter (Skarżyńska 1995) with characteristics closely related to the coal extracted in a particular basin. Apart from the initial composition, a significant factor affecting the elemental composition of coal waste is weathering and self-heating. The wide occurrence of self-heating in the LSCB and USCB and its impact on coal waste and on the environment has been described earlier (e.g., Ciesielczuk et al. 2014; Misz-Kennan et al. 2013; Misz-Kennan and Fabiańska 2011; Nádudvari and Fabiańska 2016; Pierwoła et al. 2018). In this study, it is assumed that the elements in the water come exclusively from the leaching of coal waste.

Elements such as Si, K, Ca, Fe, Na, Mg and Al in bituminous coals belong to the so-called ash-forming elements present in sedimentary rocks in amounts $> 0.5\%$ (Clark values: Si 25.48%, K 2.30%, Ca 2.87%, Fe 3.94%, Al 0.82%, Mg 1.54%, Al 6.80%; Goldschmidt, 1954; Ketris and Yudovich, 2009). P, S, Sr, Mn, and Ba occur in sedimentary rocks in quantities from 0.50%–0.01% (Clark values: P 0.061%, S 0.20%, Mn 0.074%, Sr 0.027%, Ba 0.047%). In coals, B, Cd, Cr, Cu, Li, Pb, and Zn are trace elements which occur in quantities $< 0.01\%$ or even $< 0.0001\%$ in sedimentary rocks (Clark values: B 0.0086%, Cd 0.0025%, Cr 0.0078%, Cu 0.0037%, Li 0.0055%, Pb 0.00175%, Zn 0.0079%; Hatch and Rastall 1965; Wedepohl et al. 1969; Yudovich and Ketris 2002).

The carrier of ash-forming elements in coals is biogenic ash. These are organometallic combinations of salts, carbonates, sulphates, and oxides containing large amounts of K, Na, and Ca. These are soluble compounds containing admixtures of biogenic elements such as B, Co, Mo, Mn, and Cu (Yudovich and Ketris 2002, 2015).

The sorption ash in coal consists of humic- and fulvic acids together with their salts as well as metal chelates with organic ligands. The main components of this ash are Ca, Mg, Al, Fe, and Si, typomorphic elements largely associated with the organic substance of the coals. Compared to

sedimentary rocks, some coals are significantly enriched in them. The coefficients of coal enrichment are: Cu 5.2, Ba 3.3, Sr 1.3, Mn 0.8, B 18.1, Pb 12.0, Zn 2.1, Cr 1.6, and $S > 2$ (Yudovich and Ketris, 2015). In our study, the main ash elements leached were Al, B, Ca, K, Mg, Mn, Na, P, S, and Si, i.e., elements present in higher concentrations both in coals and gangue rocks. The elution series of the elements determined for the coal-waste dump waters from the highest to the lowest concentration are as follows:

LSCB: $S > Ca > Mg > K > Na > Si > Al > P > Sr > B > Ba > Zn > Fe > Li > Mn > Cu$.

$Pb (< 0.0903 \text{ mg/dm}^3) > Cr (< 0.0028 \text{ mg/dm}^3) > Cd (< 0.0005 \text{ mg/dm}^3)$.

USCB-K: $S > Na > Ca > Mg > K > Si > Sr > B > Zn > Al > Li > P > Ba > Mn > Cu > Fe$.

$Pb (< 0.0903 \text{ mg/dm}^3) > Cr (< 0.0028 \text{ mg/dm}^3) > Cd (< 0.0005 \text{ mg/dm}^3)$.

USCB-R: $S > Na > Mg > Ca > K > Sr > Li > Si > B > Mn > Ba > P > Zn > Al > Cu$.

$Pb (< 0.0903 \text{ mg/dm}^3) > Cr (< 0.0028 \text{ mg/dm}^3) > Cd (< 0.0005 \text{ mg/dm}^3)$.

Elements most heavily leached from all the coal-waste dumps are S, Ca, Mg, Na, K, and Si. Not leached are Cd, Cr, and Pb.

Water from the USCB-R dumps contains significantly higher concentrations of the elements studied, e.g., S concentrations are a few tens of times higher than in the LSCB dump waters. Similar patterns hold for most other elements (Na, Mg, K, Li, Mn, B, Ba, Ca, and Sr; Tables 2 and 3). However, there is no real impact of sulphate leaching on pH values as only two Anna dump samples, A6 and A7, show a slight shift from neutral to more acid values of 6.40 and 6.86, respectively (Table 2S in Supplementary Material). These samples are also the poorest in elements leached. The buffering ability of carbonate ions is possibly responsible for the neutral pH and for preventing acid drainage from these dumps.

Of the ions studied, SO_4^{2-} , Cl^- , and HCO_3^- are leached to the greatest extent. The elution series of the ions determined for the dump waters from the highest to the lowest are as follows:

LSCB: $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{NO}_2^- > \text{Br}^- > \text{NH}_4^+ > \text{PO}_4^{3-}$

USCB—Katowice: $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{Br}^- > \text{F}^- > \text{NH}_4^+ > \text{NO}_2^- > \text{PO}_4^{3-}$

USCB—Rybnik: $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Br}^- > \text{NH}_4^+ > \text{F}^- > \text{NO}_2^- > \text{PO}_4^{3-}$

Phosphate(V), NH_4^+ and NO_2^- are leached to the lowest degree from coal waste. Ion concentrations in USCB-R waters are much higher than in LSCB or USCB-K waters (Tables 2 and 3). For example, in USCB-R waters, Cl^- and SO_4^{2-} concentrations are about fifty times higher

than in USCB-K waters and about four thousand times higher than in LSCB waters.

Inorganic sulphur present as sulphides in coal waste can be released and volatilized during burning as sulphur oxides. On reaction with water, sulphuric acid produced causes the formation of sulphate minerals, e.g., jarosite, alunogen or copiapite at $\text{pH} < 2.5$. Sulphuric acid reacting with carbonate rocks produces gypsum or bassanite which are ubiquitous in coal-waste dumps (Dai et al. 2008; Stracher et al. 2005; Ward 2016). Some sulphate minerals may be formed due to oxidation of coal-hosting organic sulphur rather than pyrite. Pyrite oxidation, the sequence of crystallization of Fe sulphates, and their mutual interactions, lead to the formation of highly acidic solutions rich in ferrous-, ferric- and sulphate ions and an abundance of water. The activities of metals such as K, Na, Ca, Mg and Al deriving from the gangue rocks can lead to the formation of the suite of sulphates which later undergo dehydration at different rates, depending on local humidity. Supergene products also form due to oxidation of S-rich coal-fire gases and evaporation (Kruszewski et al. 2018).

The best coal-fire fingerprint minerals are salammoniac, elemental S, rostitite, and mikasaite (Kruszewski et al. 2019b). Apart from elemental S, these minerals easily dissolve in water. Thus, high sulphur contents in water from coal-waste dumps also reflect combustion.

In the studied waters, the highest variability of occurrence for most elements is characteristic for USCB-R waters and the lowest for LSCB waters. Only Na, P, S, and Zn show greater variability in LSCB waters (Tables 2 and 3). The variability of element elution in the coal-waste dumps can be summarized in series from the highest- to the lowest value of V_x as follows:

LSCB: $\text{Mn} > \text{P} > \text{Na} > \text{S} > \text{Fe} > \text{Mg} > \text{Sr} > \text{B} > \text{Ca} > \text{Si} > \text{Zn} > \text{Al} > \text{K} > \text{Ba} > \text{Li} > \text{Cu}$.

$\text{Cd} = \text{Cr} = \text{Pb} = 0$.

USCB-K: $\text{Fe} > \text{Cu} > \text{Li} > \text{Mn} > \text{P} > \text{Zn} > \text{Si} > \text{Na} > \text{Mg} > \text{Al} > \text{Sr} > \text{B} > \text{Ba} > \text{K} > \text{S} > \text{Ca}$.

$\text{Cd} = \text{Cr} = \text{Pb} = 0$.

USCB-R: $\text{Li} > \text{P} > \text{K} > \text{Mn} > \text{Sr} > \text{Ba} > \text{Si} > \text{Al} > \text{S} > \text{B} > \text{Na} > \text{Fe} > \text{Cu} > \text{Ca} > \text{Mg} > \text{Zn}$.

$\text{Cd} = \text{Cr} = \text{Pb} = \text{Fe} = 0$.

The variability of element occurrence is high. The highest variability in all waters is for Mn and the lowest for Fe. Zinc shows high variability in occurrence in waters infiltrating the USCB dumps in the Katowice area and in the LSCB dumps, and by low variability in waters from the Rybnik dumps. Similarly, Li shows different variability of occurrence, namely, high in USCB dump- and low LSCB dumps-waters. Conversely, P and Na show low variability in USCB dump- and high variability in LSCB dump-waters.

Among the ions, the highest variability of occurrence is exhibited by Br^- and NH_4^+ whereas SO_4^{2-} which is leached in abundance from the coal-waste dumps shows low variability (Tables 2 and 3). Variations in the occurrence of ions in waters from the dumps define the following series from the highest- to the lowest value of V_x :

LSCB: $\text{PO}_4^{3-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Cl}^- > \text{Br}^- > \text{SO}_4^{2-} > \text{NO}_2^- > \text{HCO}_3^- > \text{F}^-$

USCB-K: $\text{NO}_3^- > \text{PO}_4^{3-} > \text{Cl}^- > \text{Br}^- > \text{NH}_4^+ > \text{SO}_4^{2-} > \text{F}^- > \text{HCO}_3^- > \text{NO}_2^-$

USCB-R: $\text{Br}^- > \text{Cl}^- > \text{NH}_4^+ > \text{NO}_3^- > \text{F}^- > \text{NO}_2^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{PO}_4^{3-}$

The variability in element occurrence testifies to the diversity of the material stored in the dumps and of the sources from which the elements originate as well as the degree of their binding with organic- and inorganic substances in coal or the mineral substances present. Sulphur has a lower variability of occurrence, but a much higher concentration in USCB waters, compared to LSCB waters. This may reflect a less diverse S source in the USCB dumps, but one that was undoubtedly richer in this element than that in the LSCB dumps.

Significant differences in element concentrations characterize waters emanating from burned-out dumps (LSCB) and those where self-heating is on-going. Waters from the former have much higher concentrations of the elements and ions analyzed, particularly, HCO_3^- , Cl^- and SO_4^{2-} (Table 4 and Table 5S in Supplement).

During combustion, the mineral substance of coal is enriched in elements, e.g., B, Ca, K, Mg, Mn, Na, P, S, Si and Sr from the organic matter of the coals, and are genetically bound to biogenic- and sorptive ash; they are released on combustion of the organic-carbon substance (Graf 1960; Turekian and Wedephol 1961; Yudovich and Ketris 2002). This explains the increased concentrations of these elements in the water collected in the dumps where the coal waste has been burnt-out, and their easy leaching from the coal waste by rainwater. Elements that do not show distinctive differences in concentrations between water from burnt-out and self-heating coal waste dumps are predominantly bound to waste mineral phases that, being more stable and less soluble, will not be leached easily.

The diversity in the element concentrations and the variability of occurrence of elements present in the coal-dump waters reflect the diversity of the waste stored in dumps in both basins and some inter-basin differences.

4.2 Impact of thermal activity on the composition of coal-waste dump water

There is an evident relationship between thermal activity, water conductivity, and concentrations of trace elements and ions in coal-waste dump water. Regional variations in

Table 4 The content and variability of the occurrence of main ions and trace elements in the coal-waste dumps water related to thermal activity within a dump in the LSCB

Element	Self-heating		Burned out	
	Arithmetic average	Coefficient of variation	Arithmetic average	Coefficient of variation
	X_{ar} (ppb)	V_x (%)	X_{ar} (ppb)	V_x (%)
Al	100.42	148.66	312.5	4.3
B	131.30	127.82	132	56.78
Ba	49	102.10	50	59.4
Cd	0.49	–	0.49	–
Cr	2.80	–	2.8	–
Cu	3.80	–	4.9	31.75
Fe	17.53	150.48	20.15	125.28
Li	20.67	47	16.5	21.43
Mn	5	–	16	97.23
P	27.60	–	281	132.36
Pb	90.30	–	90.3	–
Sr	182.67	118.22	147	46.18
Zn	37.90	89.14	39.85	130.77
NH ₄ ⁺	36.67	173.21	65	141.42
F ⁻	541.33	54.02	675.5	42.6
NO ₃ ⁻	256.33	87.05	138	4.1
PO ₄ ³⁻	5.67	173.21	6.5	141.42
	X_{ar} (ppm)	V_x (%)	X_{ar} (ppm)	V_x (%)
Ca	62.34	103.64	42	3.37
K	4.70	120.25	5.5	90
Mg	17	139.08	14.5	43.89
Na	4.70	171.44	3.5	141.42
S	102.34	110.04	42.5	18.3
Si	2.85	110.67	3.81	100.17
HCO ₃ ⁻	220	52.06	112.5	11.94
Cl ⁻	11.28	102.67	4.17	55.04
Br ⁻	0.04	173.21	0.1	15.56
NO ₃ ⁻	3.54	109.15	0.51	76.94
SO ₄ ²⁻	104.33	101.93	23	79.93

concentrations can be explained by regional differences in thermal activity.

The frequency and intensity of self-heating varies greatly within the USCB. The area most affected by heating is the southwestern part of the basin, i.e., the Rybnik area where almost all coal-waste dumps were or are self-heating (Fig. 1b; Misz-Kennan et al. 2013; Nádudvari 2014; Nádudvari and Ciesielczuk 2018). There, self-heating temperatures can be extremely high, e.g., 1300 °C in the Szarlota dump in Rydułtowy. Heating also affect large

areas (Misz-Kennan 2010; Misz-Kennan and Fabiańska 2010; Misz-Kennan and Tabor 2015). Though the northern part of the basin exhibits a lower intensity of heating, self-heating is common there and difficult to extinguish (Misz-Kennan and Tabor 2015). The eastern part of the basin, sometimes called the Upper Vistula Coal Basin, shows the least intensity of heating; to our knowledge, only two short, local heating episodes have occurred there. This regional pattern can be explained by differences in organic matter coalification. The westernmost part of the basin contains coals of a much higher rank ($R_o < 1.0\%$) than the easternmost part ($R_o < 0.50\%$; Jureczka and Kotas 1995). As average temperatures within the coal-bearing Mudstone Series ranging from 24.9 °C in the eastern part to 58.9 °C in the southwestern part reflect the geological history of the basin (Kędzior et al. 2007; Kędzior 2015), it is no surprise that coal-waste organic matter shows the same trend in thermal maturity. Higher coalification implies better combustion, important in the later stages of burning.

A significant factor is methane in the USCB rocks. To date, its role in the spontaneous ignition of coal waste has not been fully appreciated. Methane can promote the process in coal mines (e.g., Xia et al. 2015). There are regional differences in CH₄ occurrence in USCB coal seams. During the Mesozoic and Paleogene, coal seams in the northern- and central (Katowice area) parts of the basin were degassed. The south-western part of the USCB, characterized by an upper secondary zone beneath the Miocene cover and a primary zone at greater depth, contrasts with the south-eastern part of the basin with variable CH₄ contents (Kędzior et al. 2013). The fact that the general pattern of CH₄ content accords with the regional pattern of thermal activity within the dumps suggests that CH₄ content may be a significant factor in self-heating. Possibly, ignition in the dumps is caused by oxygen reacting with CH₄ desorbed from pores as in coal mines (Xia et al. 2014). Thus, combined CH₄-coalification factors, with CH₄ affecting ignition and coalification promoting continued burning, are reflected in the self-heating regional pattern.

LSCB coal-waste dumps show a much lower level of thermal activity than those in the USCB. Many dumps there are burnt out and now show temperatures close to ambient (Fig. 1a). Thus, expressions of thermal activity are the lowest in the LSCB, highest in the USCB-R, and intermediate in the USCB-K area.

Variation in thermal activity is followed closely by that of water conductivity and concentrations of trace elements and ions in water. Conductivity is, on average, highest (17 889 μS/cm) in the USCB-R area, lowest (425 μS/cm) in the LSCB, and intermediate (2321 μS/cm) in the the USCB-K area (Table 2S in Supplement Material). The exceptionally high conductivity of the Dębieńsko dump water (DEB samples) is related to local saline input.

Table 5 Correlation matrix for permanent and temporary water reservoirs

	Permanent water reservoir													Temporary water reservoir													
	Al	B	Ba	Ca	Cu	Fe	K	Li	Mg	Mn	Na	P	S	B	Ba	Ca	Fe	K	Li	Mg	Na	S					
<i>Spearman's rank-order correlation among elements</i>																											
B	-0.65																										
Ba	-0.53																										
Ca	-0.83	0.83	0.44																								
Cu		0.58	0.54																								
Fe			-0.50																								
K	-0.79	0.95	0.51	0.91	0.54																						
Li	-0.78	0.94	0.50	0.89	0.54																						
Mg	-0.72	0.92		0.83					0.99																		
Mn	-0.66	0.83		0.75				0.93	0.90																		
Na	-0.88	0.85	0.50	0.86			0.83	0.83	0.75								0.84	-0.54									
P		0.50					0.94	0.94	0.90	0.79							0.54										
S		0.78		0.62			0.71	0.69	0.87	0.59	0.73	0.62					0.83		0.55	0.77	0.76						
Sr	-0.85	0.83		0.93	0.54		0.90	0.89	0.76	0.77	0.90	0.60					0.83		0.62	0.72	0.72						
Zn					0.57	-0.57																					
<i>Spearman's rank-order correlation among elements and ions</i>																											
Al	-0.78			-0.78	-0.85	-0.89	-0.87	-0.87	-0.64																		
B	0.63			0.80	0.86	0.84	0.88	0.88	0.67				0.81														
Ba	0.70			0.60	0.54																						
Ca	0.55			0.88	0.82	0.96	0.88	0.88	0.61				0.68														
Cu	0.50			0.54	0.50	0.58	0.54	0.54																			
K	0.70			0.89	0.91	0.93	0.95	0.95	0.74				0.76														
Li	0.71			0.87	0.92	0.93	0.96	0.96	0.79				0.73														
Mg	0.57			0.81	0.82	0.87	0.86	0.86	0.62				0.87														
Mn	0.71			0.62	0.75	0.76	0.80	0.80	0.69				0.54														
Na	0.75			0.84	0.93	0.93	0.95	0.95	0.72				0.71														
P													0.56														
S	0.28			0.59	0.60	0.65	0.63	0.63					0.90														
Si				0.51																							
Sr	0.68			0.86	0.89	0.93	0.91	0.91	0.59				0.63														

Table 5 continued

	NH ₄ ⁺	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	NH ₄ ⁺	HCO ₃ ⁻	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻
<i>Sperman's rank-order correlation among ions</i>												
HCO ₃ ⁻	-0.58							0.60				
F ⁻	0.64						0.60					
Cl ⁻	0.82	0.79								0.81		
NO ₂ ⁻	0.66	0.87	0.91				0.55			0.85		
Br ⁻	0.75	0.80	0.97	0.95			0.65			0.64		0.63
NO ₃ ⁻	0.74	0.56	0.79	0.72	0.82			0.68		0.59		
SO ₄ ²⁻		0.78	0.58	0.66	0.61	0.31					0.86	

Since water conductivity is directly related to concentrations of ions present, it follows that the USCB-R samples contain the highest average concentrations of K, Mn, Sr, Ca, B, Mg, Na, S, NH₄⁺, NO₂⁻, NO₃⁻, Cl⁻, Br⁻, F⁻ and SO₄²⁻ (Fig. 3; Table 2) with those of Ca, K, Mg, Na, S, and NH₄⁺ many times higher than in other regions. Much milder thermal activity is registered in the USCB-K area and its waters show lower concentrations than are found in the USCB-R area. The lowest dump temperatures, and the least thermal activity, characterize the LSCB dumps as do the lowest element concentrations of elements and ions in dump waters.

There is no evident regional pattern of pH values. Most of the waters are slightly basic (7.20), the lesser numbers slightly acidic (6.80). Two Waleska samples (WA) showed higher pH values of 8.29 and 9.00, possibly reflecting water input from other than coal-waste dump sources.

4.3 Correlations between trace metals and ions

The element concentrations in coal-waste dump waters were examined for potential mutual relationships between elements and between elements and leached ions. The values of correlation coefficients between elements and between elements and ions in permanent- and temporary reservoirs, and for individual regions, were considered. In evaluating the results, correlation coefficients with values > 0.500, both negative and positive, were taken into account. Of note is the difference between the structures of the correlations in the USCB-R (36 significant correlations), the USCB-K (19 significant correlations) and the LSCB waters (9 significant correlations). The structure is understood as a network of mutual correlation relationships between the concentrations of individual elements and ions (Table 5 and Table 7S in Supplementary Material).

There are much more significant correlations between elements in waters from permanent reservoirs (62 correlations) compared to waters from temporary reservoirs (38 correlations) (Table 6; all correlations are shown in Table 6S in Supplementary Material). In the permanent water reservoirs, an additional factor meriting consideration is the precipitation of dissolved ions and, following such, the development of a state of balance between water and sediment. The higher number of correlations found for the permanent water reservoirs testifies that even well-soluble ions such as Na⁺ and Li⁺ achieved such balance. However, a longer time is required to achieve it than is provided by the temporary reservoirs on dump surfaces.

The co-occurrence of the elements in the coal-waste dump waters suggests the possibility of their relationships, both when it comes to their genesis and their participation in the general composition of the coal waste. The empirical determination of these relationships and their theoretical

Table 6 continued

W/Ions	NH ₄ ⁺	F ⁻	Cl ⁻	NH ₄ ⁺	F ⁻	Cl ⁻	Ions	NH ₄ ⁺	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻
<i>Sperman's rank-order correlation among ions</i>													
NO ₂ ⁻		0.93					HCO ₃ ⁻						
Br ⁻	0.88			-0.78		0.89	F ⁻	0.69					
NO ₃ ⁻			0.86			0.63	Cl ⁻	0.77	0.96				
							NO ₂ ⁻	0.64	0.97	0.93			
							Br ⁻	0.70	1.00	0.98	0.97		
							NO ₃ ⁻	0.78	0.89	0.90	0.84	0.90	
							SO ₄ ²⁻	0.22	0.70	0.67	0.63	0.70	0.54

justification is a complex problem. Certain systems of correlations are characteristic not only for the given elements but also for specific geochemical environments.

In the structure of the correlations, there are eleven significant triads, characterized by high positive correlation coefficients. These triads form closed systems of Ca-Na-Mg-Ca, Ca-B-K-Sr, Ca-Sr-Li-Ca, Ca-K-Na-Ca, Ca-Sr-Na-Ca, Ca-B-Sr-Ca, Ca-B-Na-Ca, Ca-B-Mg-Ca, Ba-B-Li-Ca, Ca-K-Mg-Ca, and Ca-Li-Na-Ca (Fig. 4). Not all correlations within the established structures are an expression of simple and unambiguous dependencies. Closed triads are formed by elements from the first- and second group of the periodic table. These are elements that easily form compounds and constitute the main components of rock-forming minerals. Their Clark in sedimentary rocks is 0.5% (Turekian and Wedepohl 1961). They form soluble compounds with chloride, nitrate (V), and sulphate (VI) ions. This is reflected in the high values of correlation coefficients between these elements and ions.

The activity of hydrogen ions in natural waters has a very significant impact on geochemical processes in these environments and the possibility of the occurrence of various chemical elements in them. The importance of pH for geochemical processes reflects the fact that different metals precipitate as hydroxides at different pH values. It plays an important role during the migration of various elements including such a common element as iron, in surface waters, and thus during hypergenic processes. The Fe solubility in water at pH = 6 is about 100,000 times greater than at pH = 8.5 (White 2013). Similarly, the separation of SiO₂ and Al₂O₃ occurring in weathering is the result of the dissimilar solubility of these compounds at various pH in the aqueous environment. In strongly acidified environments with pH < 4, Al₂O₃ is mobilized and SiO₂ is immobile, but in aquatic environments where pH lies in the range from 5–9 (as in the samples investigated here), Al₂O₃ is immobilized but SiO₂ is increasingly

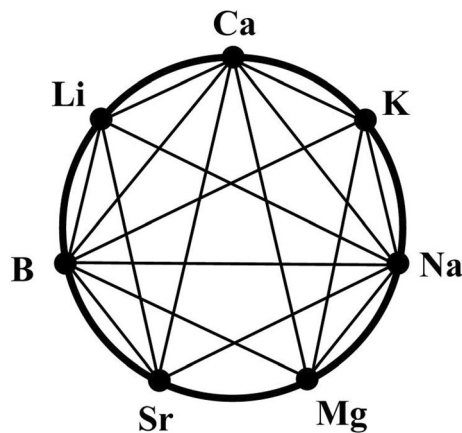


Fig. 4 Correlations between element triads

soluble with increasing pH (White 2013). This caused the negative Al-Si correlation (Tables 6 and 7S in Supplementary Material).

Another important factor affecting element dissolution and migration under hypergenic conditions is the oxidation–reduction potential. For example, Fe requires a lower E° potential for the Fe^{2+} transition to Fe^{3+} and, thus, oxidizes faster than Mn during their joint migration and precipitating as a hydroxide. Oxidation of Mn^{2+} to Mn^{4+} requires a higher potential and can only occur after Fe oxidation. Therefore, the Mn (IV) will precipitate later and in another place (White, 2013). This can explain the negative correlations between Mn and Fe in waters from permanent reservoirs, $r = -0.47$ (Table 6Sa in Supplementary Material). Mn and Fe are also negatively correlated in the USCB-R waters.

The correlation structure between element concentrations in permanent- and temporary reservoirs is different. For permanent reservoirs, there are correlations between the typomorphic elements that have a high affinity for organic substances, e.g., Ba-Cu (0.576), B-Mn (0.833) and Cu-Zn (0.567). Such relationships do not occur in temporary reservoirs. Additionally, in the permanent reservoirs, there are negative correlations between all the elements determined and Al, possibly due to pH values close to neutral that promote Al immobilization but allow many elements to be mobilized.

On the basis of recent research on the chemical- and mineralogical composition of Upper Silesia waste rocks (Ciesielczuk et al. 2014) and on attempts to leach elements from Upper Silesian coal waste (Pierwoła et al., 2018), it can be concluded that elements in waters were leached from rocks and minerals transformed as a result of hypergenesis or dump fires. Elements such as Mg, K, Ca, Na, Mn, Fe, Cu, Cd, Pb, and Co occur in coal waste in concentrations ranging from 12–98,600 mg/kg. These rocks leaching delivered solutions with concentrations of 0–565 mg/kg. The highest concentrations were found for Fe, Ca, K, Na and Mg, and the lowest for Cu and Co. Cd and Pb (0 mg/kg) were not leached whereas Ca (565 mg/kg), K (109 mg/kg) and Mg (49 mg/mL) show the highest concentrations. In some samples, the concentrations of K, Mg, and Ca are much higher, e.g., for Ca they reach 13,300 mg/kg, for K 1060 mg/kg, and Mg 1090 mg/kg. The percentage of leached concentrations varies from 0% to 4.55%. Only for Ca, K, and Mg are concentrations higher (8.43%–41.26%; Pierwoła et al. 2018). The values indicate minor leaching of the elements from the rocks mineral fraction. There must be another factor, namely, organic material that carries the given elements. Thus, the chemical composition of coal-waste dump water is related to the origin of elements in the material stored, the manner in which elements occur in this material, their affinity to

organic- and mineral phases, and to the geochemical environment and the stage of hypergenesis.

Several factors related to self-heating cause an increase in element concentrations in dump waters. Self-heating results in the formation of pyrolytic water in rock particles. It, as does rainwater seeping through the dump, acts as a solvent forming solutions rich in elements (e.g., Chen et al. 2008). High temperatures promote cracking of coal-waste fragments aiding water penetration into their interiors, promoting further dissolution of rock elements. On a larger scale, fissures and vents formed in dump surfaces allow rainwater to enter dump interiors. Apart from the increase of coal-waste surface accessible to water, heating also induces changes in mineral composition (Ciesielczuk et al. 2014; Pierwoła et al. 2018).

The regional pattern of element concentrations confirms their origin from coal waste and not from, e.g., atmospheric particulate matter (APM) as is the case with organic contamination in these waters (Fabińska et al. 2020). USCB and LSCB are regions of high levels of APM emission from both road traffic and bituminous-coal combustion (Klejnowski et al. 2010). However, APM mineral phases are mostly composed of insoluble compounds such as metal oxides or metal alloys (Jabłońska and Janeczek 2019). Thus, their metals are not transferred to waters in amounts comparable to those leached from coal waste. The only exceptions are Ba sulphate and Fe, Pb, and Cd sulphides. As Ba, Li, and Cu, (in a few samples only) concentrations do not follow the regional pattern, it is tentatively assumed that they mostly come from atmospheric sources. An additional indicator of atmospheric input comes from the cluster analysis (Fig. 5). Both temporary- and permanent reservoirs show a tendency to form clusters reflecting their localization; the closest are the reservoirs from the same dump, e.g., all Dębieńsko waters (Deb) or from the same area, e.g., WA1 and P1. The pattern is preserved whether ions and trace metals are considered separately or together.

Other components that do not follow the regional pattern are Fe, P, Si, and among ions, HCO_3^- . Bicarbonate ion concentration in water is mainly governed by pH to form the balance with CO_2 (gas) and CO_3^{2-} . Thus, it may be surmised that even if self-heating promoted its dissolution, subsequent CO_3^{2-} precipitation changed concentrations to such an extent that the regional pattern was obscured.

4.4 Impact of reservoir size on element concentrations

Water reservoirs on coal-waste dumps and in their vicinity can be permanent (ponds, streams) or temporary (puddles). Typically, concentrations of ions and major and trace elements are much lower in the latter as they dry up after a

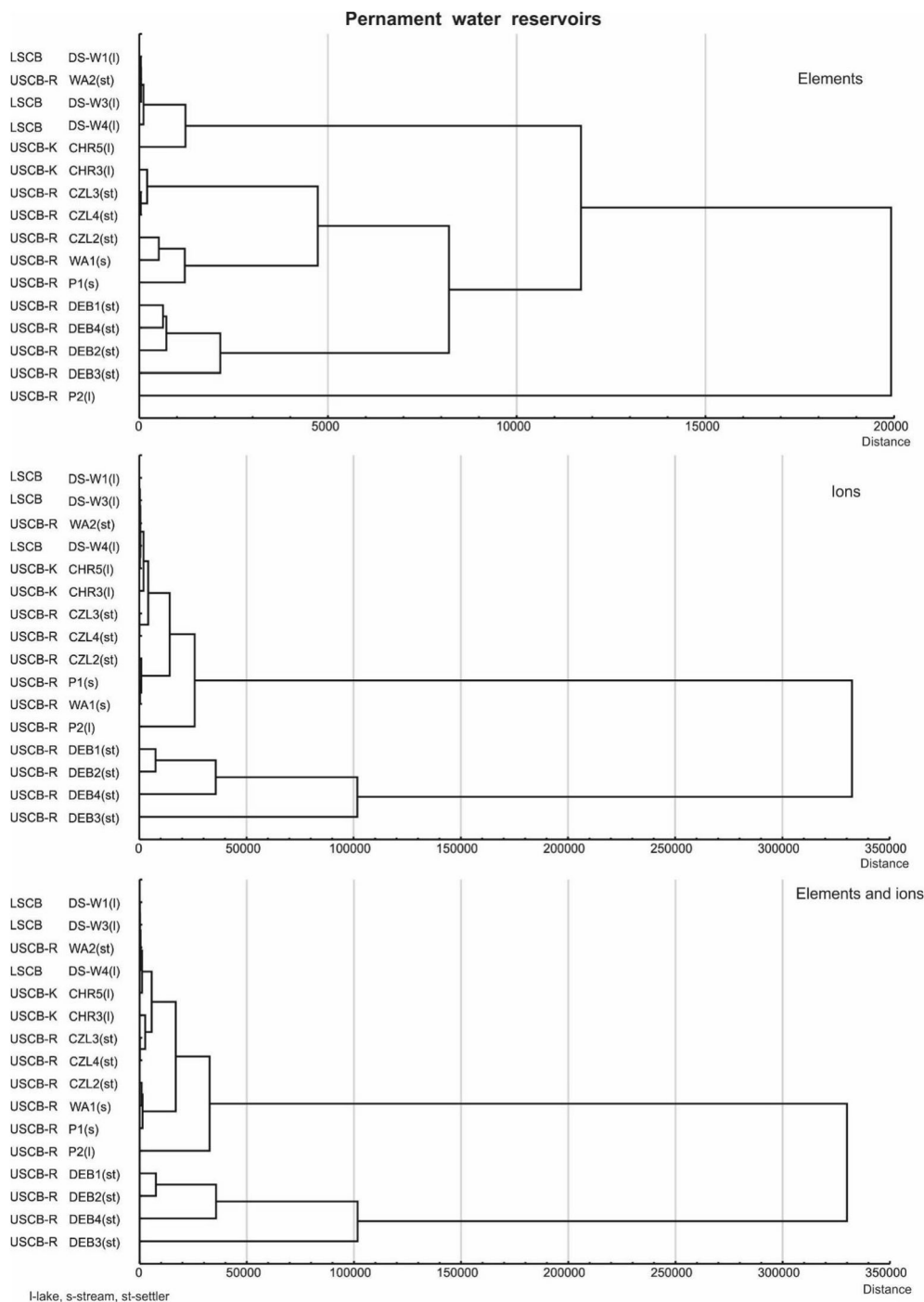


Fig. 5 Pattern (dendrogram) of the main ion- and trace-element concentrations in **a** permanent reservoirs and **b** temporary reservoirs

short period; there is less time to leach the elements and achieve a balance in concentrations between rock and water.

In both types of reservoirs, S shows the highest and most diverse concentration values. Other high-concentration elements are Na, Ca, and Mg (Tables 3 and 4S in Supplementary Material; Fig. 6).

Concentrations of K are high in permanent reservoirs (< 1453 ppm) and, in temporary reservoirs, much lower (< 30 ppm). Elements with low concentrations (< approx. 1000 ppb) in both types of reservoirs are Cu, Fe, Zn, Al, and P. Ba and B concentrations discriminate between reservoir types; in permanent reservoirs, concentrations are > 1000 ppb, in temporary reservoirs, < 1000 ppb. Li also displays a significant difference in concentrations in

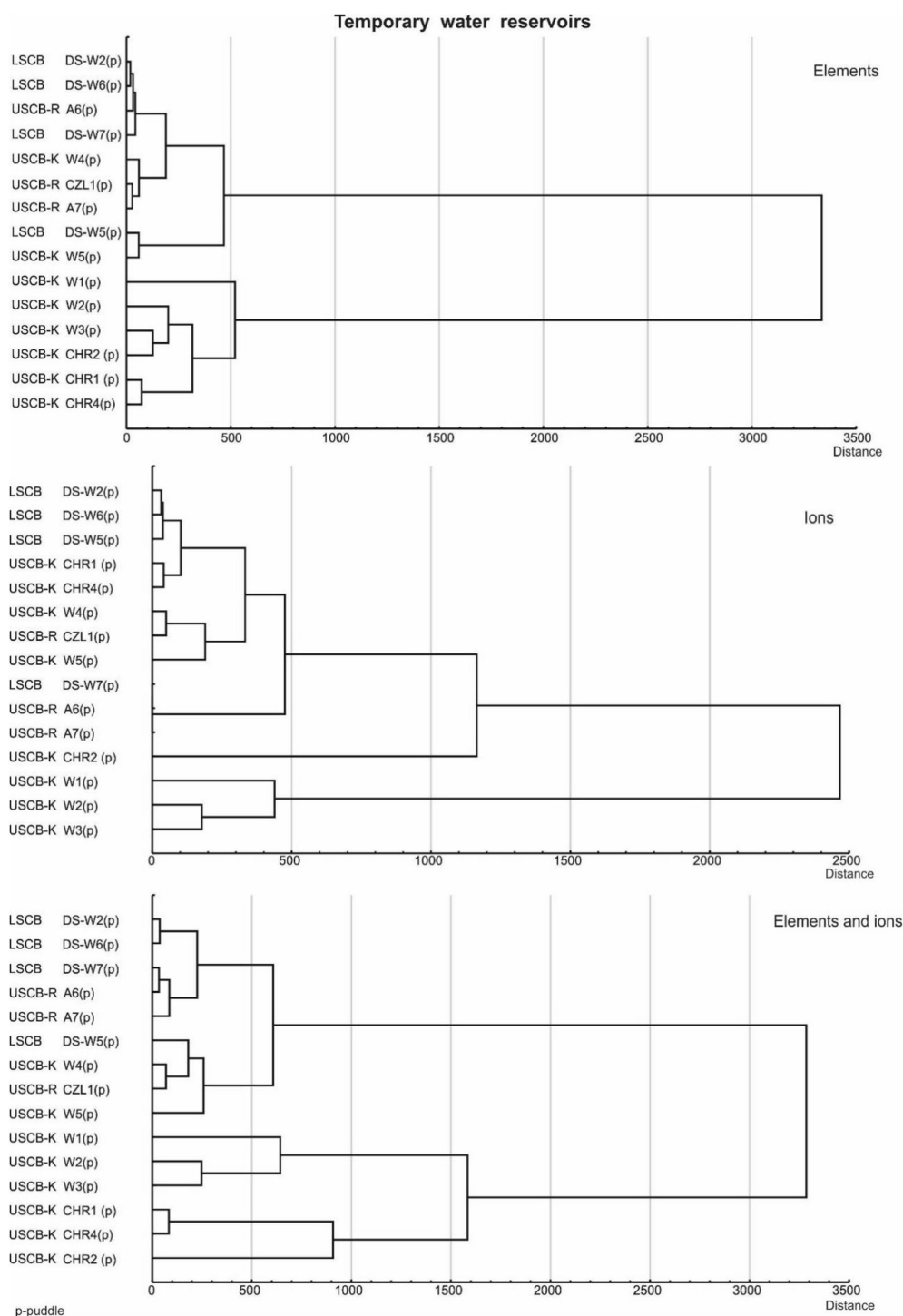


Fig. 5 continued

temporary reservoirs containing 2–98 ppb and in permanent reservoirs, < 33,370 ppb (Tables 3 and 4S in Supplementary Material; Fig. 6). Significant values of the coefficient of variation (mostly > 50%) indicate significant variation in element concentrations in both types of the reservoir with a larger number of elements showing the

lowest variation at the lowest concentrations and the largest variation at the highest. Ions with lower concentrations are PO_4^{3-} , NH_4^+ , NO_2^- , F^- , and Br^- . Ions with higher concentrations are NO_3^- , Cl^- , HCO_3^- , and SO_4^{2-} .

The concentrations of the elements determined in the coal-waste waters are mostly much higher than legally

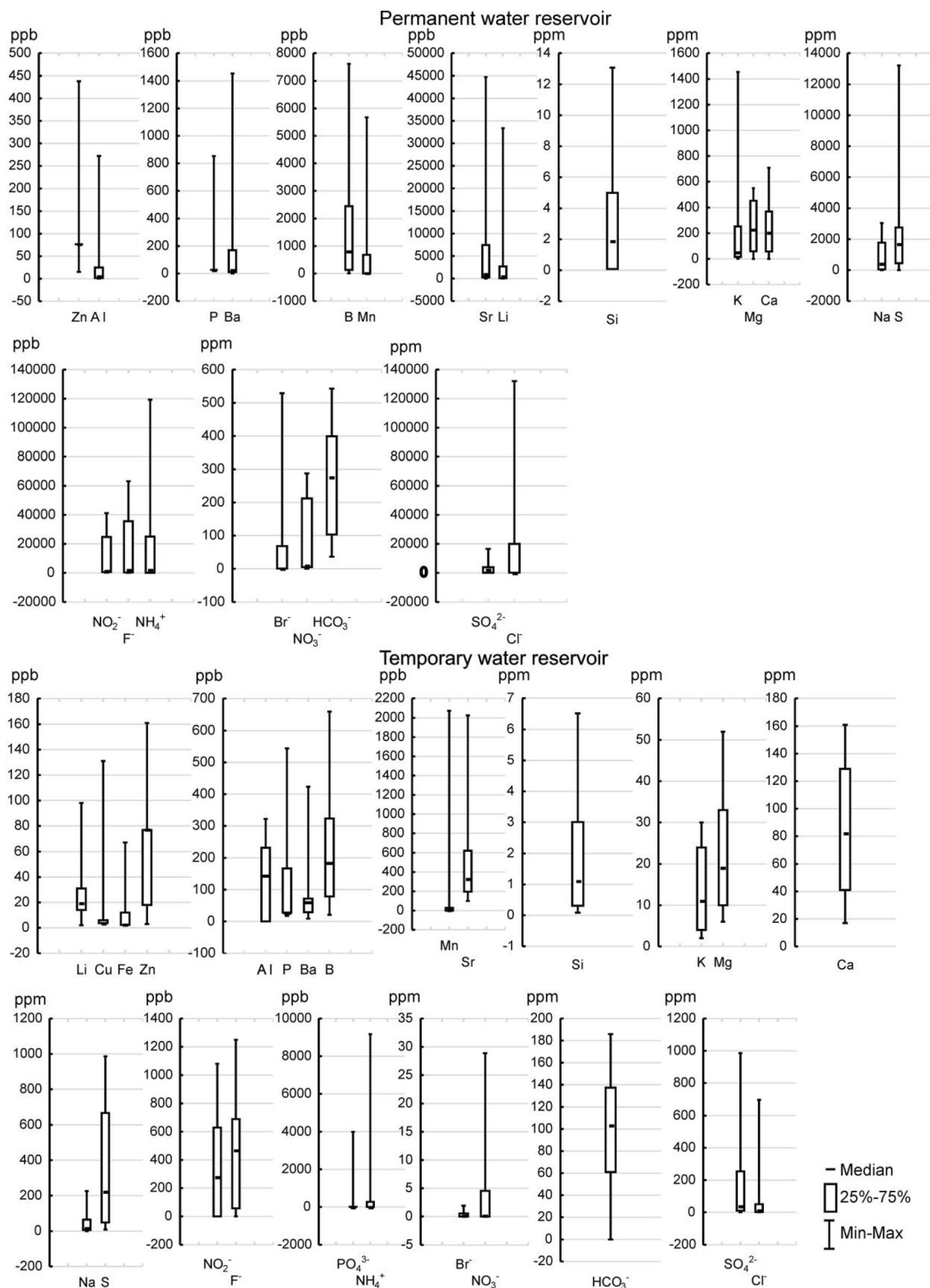


Fig. 6 Box-whisker plots of main ion- and trace-element concentrations for permanent- and temporary water reservoir

allowable concentration levels in the wastewater discharged into surface waters and the ground. Acceptable concentrations were observed only in 12 samples out

of 31, i.e., 4 from USCB-R, 3 from LSCB, and 5 from USCB-K. Only 5 samples (3 from LSCB and 2 from USCB-R) had contents of analyzed elements demanded for

drinking water. Of course, to qualify water as drinking water or non-invasive wastewater, a number of additional conditions must be met that were not considered in this research.

5 Conclusions

(1) Coal-waste dump waters show differences in concentrations of elements such as Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, Pb, S, Si, Sr and Zn, and of ions such as NH_4^+ , HCO_3^- , F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} .

(2) The highest concentrations in the dump waters are shown by S, Na, Ca, and Mg and the lowest by Cu. The highest ion concentrations are shown by SO_4^{2-} , Cl^- and HCO_3^- and the lowest by PO_4^{3-} , NH_4^+ and NO_2^- . The highest element concentrations occur in dump waters in the Rybnik area and the lowest in waters from LSCB dumps which also lack Cd, Cr, and Pb.

(3) The highest average variation of occurrence (> 100%) is characteristic for Na, Mn, Al, and Zn, and the lowest (< 50%) for Cu and Fe. Among the ions, the highest variability was shown by Br^- and NH_4^+ , and the lowest by PO_4^{3-} , HCO_3^- and SO_4^{2-} .

(4) Differences in the element concentrations and variability of occurrence in the dump waters reflect the diversity of the coal-waste material stored in dumps in the USCB and LSCB and are indicative of various genetic factors that shaped the elemental composition of the coal-waste. There are significant differences in element concentrations between waters from burnt-out dumps and those currently self-heating. Waters from burnt-out dumps show much higher element- and ion concentrations.

(5) Concentrations of ions and trace elements are relatively much lower in the temporary reservoirs that exist on dump surfaces for short periods (weeks).

(6) There is a clear relationship between the concentrations of trace elements and ions in dump waters and thermal activity within dumps; a regional pattern of trace element- and ion concentrations is explained by regional differences in thermal activity. The highest concentrations occur in the Rybnik area where the thermal activity is currently the greatest and the lowest in LSCB reservoirs where the activity is low and waning.

(7) Concentrations of the elements determined in the coal-waste waters far exceed, in most cases, those allowed in non-invasive wastewater discharged into surface waters or the ground.

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Data availability The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Declarations

Conflict of interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Baruah MK, Kotoky P, Baruah GC (2003) Distribution and nature of organic/mineral bound elements in Assam coals. *Fuel* 82:1783–1791. [https://doi.org/10.1016/S0016-2361\(03\)00107-8](https://doi.org/10.1016/S0016-2361(03)00107-8)
- Bojarska K, Bzowski Z (2012) Test results of water extracts of extractive waste from the coal mines of the Upper Silesian Coal Basin in the aspect of environmental impact. (In Polish: Wyniki badań wyciągów wodnych odpadów wydobywczyc z kopalń węgla Górnosląskiego Zagłębia Węglowego w aspekcie wpływu na środowisko). *Górnictwo i Geologia* 7(2):101–113
- Bossowski A (1995) Coal deposits. lower Silesian coal basin. In: Zdanowski A, Żakowa H (eds) *The Carboniferous System in Poland*. Publication of Polish Geological Institute, Warsaw, pp 173–175
- Chen Y, Liu G, Le W, Yu K, Yang J (2008) Occurrence and fate of some trace elements during pyrolysis of Yima coal, China. *Energy Fuels* 22:3877–3882. <https://doi.org/10.1021/ef800485w>
- Ciesielczuk J, Misz-Kennan M, Hower JC, Fabiańska MJ (2014) Mineralogy and geochemistry of coal wastes from the

- Starzykowiec coal-waste dump (Upper Silesia, Poland). *Int J Coal Geol* 127:42–55. <https://doi.org/10.1016/j.coal.2014.02.007>
- Dai S, Ren D, Zhou Y, Chou C-L, Wang X, Zhao L, Zhu X (2008) Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan Coalfield, Yunnan, China: evidence for a volcanic ash component and influence by submarine exhalation. *Chem Geol* 255:182–194. <https://doi.org/10.1016/j.chemgeo.2008.06.030>
- Dai S, Ren D, Chou C-L, Finkelman RB, Seredin VV, Zhou Y (2012) Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. *Int J Coal Geol* 94:3–21. <https://doi.org/10.1016/j.coal.2011.02.003>
- Dai S, Seredin VV, Ward CR, Jiang J, Hower JC, Song X, Jiang Y, Wang X, Gornostaeva T, Li X, Liu H, Zhao L, Zhao C (2014) Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. *Int J Coal Geol* 121:79–97. <https://doi.org/10.1016/j.coal.2013.11.004>
- Dai S, Wang X, Zhao L (2017) Mineral Matter and Trace Elements in Coal. MDPI AG, Switzerland. <https://doi.org/10.3390/books978-3-03842-623-3>
- Fabiańska MJ, Ciesielczuk J, Kruszewski Ł, Stracher G, Moszumańska I (2013) Gaseous compounds and efflorescences generated in self-heating coal-waste dumps—a case study from the Upper- and Lower Silesian Coal Basins (Poland). *Int J Coal Geol* 116–117:247–261. <https://doi.org/10.1016/j.coal.2013.05.002>
- Fabiańska M, Misz-Kennan M, Ciesielczuk J, Kruszewski Ł (2016) Comparison of geochemical, petrographical and mineralogical properties of oxidized and unoxidized coal wastes from Lower Silesian Coal Basin (Poland). Abstracts from a joint meeting of TSOP - ICCP - AASP, Houston, Texas USA, pp 52–53
- Fabiańska MJ, Ciesielczuk J, Nádudvari Á, Misz-Kennan M, Kowalski A, Kruszewski Ł (2018) Environmental influence of gaseous emissions from self-heating coal waste dumps in Silesia, Poland. *Environ Geochem Health* 41:575–601. <https://doi.org/10.1007/s10653-018-0153-5>
- Fabiańska MJ, Nádudvari Á, Ciesielczuk J, Szram E, Misz-Kennan M, Więclaw D (2020) Organic contaminants of coal-waste dump water in Lower- and Upper Silesian Coal Basins (Poland). *Appl Geochem* 122: <https://doi.org/10.1016/j.apgeochem.2020.104690>
- Finkelman RB (2004) Potential health impact of burning coal beds and waste banks. *Int J Coal Geol* 59:19–24. <https://doi.org/10.1016/j.coal.2003.11.002>
- Frużyński A (2012) Hard coal mines in Poland. Łódź, Publishing House, Księży Młyn
- Goldschmidt VM (1954) *Geochemistry*. Clarendon Press, Oxford
- Graf DL (1960) *Geochemistry of carbonate sediments and sedimentary carbonate rocks, part I-IVb*. Illinois State Geological Survey (of special importance; part III, Minor element distribution), pp 1–42. <https://core.ac.uk/download/pdf/17355237.pdf>
- Guo S (2018) Trace Elements in Coal Gangue: A Review. In: Al-Juboury A (Ed), *Contribution to Mineralization*, Chapter 6, pp 128–143. IntechOpen. <https://www.intechopen.com/books/contributions-to-mineralization/trace-elements-in-coal-gangue-a-review>
- Hower JC, Eble CF, Dai S, Belkin HE (2016) Distribution of rare earth elements in eastern Kentucky coals: Indicators of multiple modes of enrichment? *Int J Coal Geol* 160–161:73–81. <https://doi.org/10.1016/j.coal.2016.04.009>
- Huggins FE, Seidu LBA, Shah N, Backus J, Huffman GP, Honaker RQ (2011) Mobility of elements in long-term leaching tests on Illinois #6 coal rejects. *Int J Coal Geol* 94:326–336. <https://doi.org/10.1016/j.coal.2011.04.006>
- Jabłońska M, Janeczek J (2019) Identification of industrial point sources of airborne dust particles in an urban environment by a combined mineralogical and meteorological analyses: a case study from the Upper Silesian conurbation, Poland. *Atmos Pollut Res* 10:980–988. <https://doi.org/10.1016/j.apr.2019.01.006>
- Jureczka J, Kotas A (1995) Coal deposits. Upper Silesian Coal Basin. In: Zdanowski A, Żakowa H (eds) *The Carboniferous System in Poland*. Publication of Polish Geological Institute, Warsaw, pp 164–173
- Jureczka J, Dopita M, Gałka M, Krieger W, Kwarciański J, Martinec P (2005) Geological atlas of coal deposits of the Polish and Czech parts of the Upper Silesian Coal Basin. Polish Geological Institute, Ministry of Environment, Warsaw
- Kamińska A, Strzemieczna A (eds) (2018) *Water intended for human consumption*. Main Sanitary Inspectorate, Warsaw, Compendium (in Polish)
- Ketris MP, Yudovich EY (2009) Estimations of clarkes for carbonaceous biolithes: world averages for trace element contents in black shales and coals. *Int J Coal Geol* 78(2):135–148. <https://doi.org/10.1016/j.coal.2009.01.002>
- Kędzior A (2015) Methane contents and coal-rank variability in the Upper Silesian Coal Basin, Poland. *Int J Coal Geol* 139:152–164. <https://doi.org/10.1016/j.coal.2014.09.009>
- Kędzior A, Gradziński R, Doktor M, Gmur D (2007) Sedimentary history of a mississippian to pennsylvanian coal-bearing succession: an example from the Upper Silesia Coal Basin. *Poland Geol Mag* 144(3):487–496. <https://doi.org/10.1017/S001675680700341X>
- Kędzior S, Kotarba MJ, Pękała Z (2013) Geology, spatial distribution of methane content and origin of coalbed gases in Upper Carboniferous (Upper Mississippian and Pennsylvanian) strata in the south-eastern part of the Upper Silesian Coal Basin, Poland. *Int J Coal Geol* 105:24–35. <https://doi.org/10.1016/j.coal.2012.11.007>
- Kita S (2015) Świętochłowice: They are dismantling the large “Ajska” heap. The stench and dust, people are furious (in Polish). <https://dziennikzachodni.pl/swietochlowice-rozbieraja-wielka-halde-ajska-smrod-i-pyl-ludzie-sa-wsciekli/ar/c3-9168026>
- Klatka S, Malec M, Kruk E, Ryzek M (2017) Evaluation of possibility of natural utilisation of coal mine waste used for surface leveling (in Polish). *Acta Agrophys* 24(2):253–262
- Klejnowski K, Kozińska B, Krasa A, Rogula-Kozłowska W (2010) Polycyclic aromatic hydrocarbons in PM₁, PM_{2.5}, PM₁₀ and TSP in the Upper Silesian agglomeration. *Poland Arch Environ Prot* 36:65–72
- Klojzy-Karczmarczyk B, Mazurek J, Staszczak J (2016) Analysis of the quality of waste from coal mining in relation to the requirements for inert mining waste (in Polish: Analiza jakości odpadów z nieczynnej hałdy górnictwa węgla kamiennego w odniesieniu do wymagań stawianych odpadom wydobywczym obojętnym). *Zeszyty Naukowe Instytutu Gospodarki Surowcami Mineralnymi i Energią Polskiej Akademii Nauk* 95:227–242
- Kolker A (2012) Minor element distribution in iron disulfides in coal: a geochemical review. *Int J Coal Geol* 94:32–43. <https://doi.org/10.1016/j.coal.2011.10.011>
- Kotarba MJ, Rice DD (2001) Composition and origin of coalbed gases in the Lower Silesian basin, southwest Poland. *Appl Geochem* 16:895–910. [https://doi.org/10.1016/S0883-2927\(00\)00058-5](https://doi.org/10.1016/S0883-2927(00)00058-5)
- Kruszewski Ł (2019a) Geochemical behavior of trace elements in Silesian coal-fire gob piles. In: Stracher GB (ed) *Coal and Peat Fires A Global Perspective*, vol 5. Elsevier, Amsterdam, pp 407–450
- Kruszewski Ł (2019b) Secondary sulphate minerals from Bhanine Val ley coals (South Lebanon)—a crystallochemical and geochemical study. *Geol Q* 63(1):65–87. <https://doi.org/10.7306/gq.1450>

- Kruszewski Ł, Fabiańska MJ, Ciesielczuk J, Segit T, Moszumańska I (2018) First multi-tool exploration of a gas-condensate-pyrolysate system from the environment of burning coal mine heaps: an in situ FTIR and laboratory GC and PXRD study based on Upper Silesian materials. *Sci Total Environ* 640–641:1044–1071. <https://doi.org/10.1016/j.scitotenv.2018.05.319>
- Lewińska-Preis L, Fabiańska MJ, Ćmiel S, Kita A (2009) Geochemical distribution of trace elements in Kaffiorya and Longyearbyen coals, Spitsbergen, Norway. *Int J Coal Geol* 80:211–223. <https://doi.org/10.1016/j.coal.2009.09.007>
- Li W, Chen L, Zhou T, Tang Q, Zhang T (2011) Impact of coal gangue on the level of main trace elements in the shallow groundwater of a mine reclamation area. *Min Sci Technol (China)* 21:715–719. <https://doi.org/10.1016/j.mstc.2011.03.004>
- Misz-Kennan M (2010) Thermal alterations of organic matter in coal wastes from Upper Silesia Poland. *Mineralogy* 41(3–4):105–236. <https://doi.org/10.2478/v10002-010-0001-4>
- Misz-Kennan M, Fabiańska MJ (2010) Thermal transformation of organic matter in coal waste from Rymer Cones (Upper Silesian Coal Basin, Poland). *Int J Coal Geol* 81:343–358. <https://doi.org/10.1016/j.coal.2009.08.009>
- Misz-Kennan M, Fabiańska M (2011) Application of organic petrology and geochemistry to coal waste studies. *Int J Coal Geol* 88:1–23. <https://doi.org/10.1016/j.coal.2011.07.001>
- Misz-Kennan M, Tabor A (2015) The thermal history of selected coal waste dumps in the Upper Silesian Coal Basin (Poland). In: Stracher GB, Sokol EV, Prakash A (eds) *Coal and Peat Fires: A Global Perspective*, vol 3. Case Studies. Elsevier, Amsterdam, pp 431–474
- Misz-Kennan M, Ciesielczuk J, Tabor A (2013) *Coal-Waste Dump Fires of Poland*. In: Stracher GB, Prakash A, Sokol EV (eds) *Coal and Peat Fires: A Global Perspective Photographs and Multimedia Tours*, vol 2. Elsevier, Amsterdam, pp 233–311
- Nádudvari Á (2014) Thermal mapping of self-heating zones on coal waste dumps in Upper Silesia (Poland) - A case study. *Int J Coal Geol* 128–129:47–54. <https://doi.org/10.1016/j.coal.2014.04.005>
- Nádudvari Á, Ciesielczuk J (2018) Remote Sensing Techniques for Detecting Self-Heated Hot Spots on Coal Waste Dumps in Upper Silesia, Poland - Chapter 18. In: Stracher GB (Ed), *Coal and Peat Fires: A Global Perspective: Volume 5: Case Studies – Advances in Field and Laboratory Research*, 1st Edition. ISBN-Hardcover: 978–0–12–849885–9, pp. 387–406.
- Nádudvari Á, Fabiańska MJ (2016) Use of geochemical analysis and vitrinite reflectance to assess different self-heating processes in coal-waste dumps (Upper Silesia, Poland). *Fuel* 181:102–119. <https://doi.org/10.1016/j.fuel.2016.04.129>
- Nádudvari Á, Fabiańska MJ, Marynowski L, Kozielska B, Koniecznyński J, Smółka-Danielowska D, Ćmiel S (2018) Distribution of coal and coal combustion related organic pollutants in the environment of the Upper Silesian Industrial Region. *Sci Total Environ* 628–629:1462–1488. <https://doi.org/10.1016/j.scitotenv.2018.02.092>
- Nowak J (2013) Rare Earth Elements (REEs) in the overburnt mining waste material. 65nd Meeting of the International Committee for Coal and Organic Petrology (ICCP). University of Silesia, Sosnowiec, Poland, pp 96–98
- Nowak J, Kokowska-Pawłowska M (2017) Changes in the concentration of some rare earth elements in coal waste. *Arch Min Sci* 62(3):495–507. <https://doi.org/10.1515/amsc-2017-0037>
- Querol X, Fernandez-Turiel JL, Lopez-Soler A (1995) Trace elements in coal and their behaviour during combustion in large power station. *Fuel* 74(3):331–343. [https://doi.org/10.1016/0016-2361\(95\)93464-0](https://doi.org/10.1016/0016-2361(95)93464-0)
- Pierwoła J, Ciesielczuk J, Misz-Kennan M, Fabiańska MJ, Bielińska A, Kruszewski Ł (2018) Structure and thermal history of the Wełnowiec dump, Poland: a municipal dump rehabilitated with coal waste. *Int J Coal Geol* 197:1–19. <https://doi.org/10.1016/j.coal.2018.08.001>
- Pone JDN, Hein KAA, Stracher GB, Annegarn HJ, Finklemann RB, Blake DR, McCornack JK, Schroeder P (2007) The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa. *Int J Coal Geol* 72(2):124–140. <https://doi.org/10.1016/j.coal.2007.01.001>
- Pusz S, Krztoi A, Komraus JL, Martinez-Tarazona MR, Martinez-Alonso A, Tascon JMD (1997) Interactions between organic matter and minerals in two bituminous coals of different rank. *Int J Coal Geol* 33(4):369–386. [https://doi.org/10.1016/S0166-5162\(96\)00052-3](https://doi.org/10.1016/S0166-5162(96)00052-3)
- Regulation of the Minister of the Environment of 15 July 2011 on the criteria for classifying extractive waste as inert waste, *Journal of Law* 2011, item 1048.
- Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption, *Journal of Laws* 2017, item 2294.
- Regulation of the Minister of Maritime Economy and Inland Navigation of 15 July 2019 on substances particularly harmful to the aquatic environment and conditions to be met when discharging wastewater into waters or into the ground, as well as when discharging rainwater or snowmelt into waters or water facilities, *Journal of Law* 2019, item 1311.
- Ribeiro J, Ferreira da Silva E, Flores D (2010) Burning of coal waste piles from Douro Coalfield (Portugal): petrological, geochemical and mineralogical characterisation. *Int J Coal Geol* 81(4):359–372. <https://doi.org/10.1016/j.coal.2009.10.005>
- Sikorska-Maykowska M (ed) (2001) *Valorization of the Natural Environment and Identification of Environmental Threats in Silesia Voivodship*. Polish Geological Institute and Marshal Office of the Silesian Voivodeship, Warsaw
- Skarżyńska KM (1995) Reuse of coal mining wastes in civil engineering—Part 1: properties of minestone. *Waste Manag* 15:3–42
- Sokol EV, Maksimova NV, Nigmatulina EN, Sharygin VV, Kalugin VM (2005) *Combustion Methamorphism*: Publishing House of the SB RAS. Novosibirsk (in Russian).
- Stanisz A (2006a) *Straightforward statistics course*, vol 1. StatStof Polska, Kraków, p 532
- Stanisz A (2006b) *Straightforward statistics course*, vol 3. StatStof Polska, Kraków, p 500
- Stracher GB, Prakash A, Schroeder P, McCormack J, Zhang X, Van Dijk P, Blake D (2005) New mineral occurrences and mineralization processes: Wuda coal-fire gas vents of Inner Mongolia. *Am Mineral* 90:1729–1739
- Swaine DJ (1990) *Trace elements in coal*. Butterworth & Co Ltd, London
- Szopka K, Bogda A, Karczewska A, Bałka B, Wojtkowiak M, Pruchniewicz D (2010) Properties of waste rock deposited on mine spoils of hard coal mines in Nowa Ruda with the perspective of their biological reclamation. *Quart Environ Eng Des* 138(18):5–11
- Turekian K, Wedepohl K (1961) Distribution of the elements in some major units of the Earth crust. *Geol Soc Am Bull* 72(2):175–191. [https://doi.org/10.1130/0016-7606\(1961\)72\[175:DOTEIS\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2)
- Ward CR (2016) Analysis, origin and significance of mineral matter in coal: an updated review. *Int J Coal Geol* 165:1–27. <https://doi.org/10.1016/j.coal.2016.07.014>
- Wedepohl KH, Correns CW, Shaw DM, Turekian KK, Zemann J (1969) *Handbook of Geochemistry*. Springer-Verlag, Berlin
- White WM (2013) *Geochemistry*. Wiley-Blackwell, UK
- Xia TQ, Zhou FB, Liu J, Kang JH, Gao F (2014) A fully coupled hydro-thermo-mechanical model for the spontaneous

- combustion of underground coal seams. *Fuel* 125:106–115. <https://doi.org/10.1016/j.fuel.2014.02.023>
- Xia TQ, Zhou FB, Gao F, Kang J, Liu J, Wang J (2015) Simulation of coal self-heating processes in underground methane-rich coal seams. *Int J Coal Geol* 141–142:1–12. <https://doi.org/10.1016/j.coal.2015.02.007>
- Xu M, Yan R, Zheng C, Qiao Y, Han JI, Sheng C (2003) Status of trace element emission in a coal combustion process: a review. *Fuel Process Technol* 85(2–3):215–237. [https://doi.org/10.1016/S0378-3820\(03\)00174-7](https://doi.org/10.1016/S0378-3820(03)00174-7)
- Yang L, Song JF, Bai X, Song B, Wang RD, Zhou TH, Jia JL, Pu HX (2016) Leaching behavior and potential environmental effects of trace elements in coal gangue of an open-cast coal mine area, inner Mongolia. *China Miner* 6(2):70–68. <https://doi.org/10.3390/min6020050>
- Younger PL (2004) Environmental impacts of coal mining and associated wastes: a geochemical perspective. In: Gieré R, Stille P, (Eds) *Energy, waste and the environment: a geochemical perspective*, *Geoll Soc Spec Publ* 236: pp 169–209. ISBN-13: 978–1862391673
- Yudovich YE, Ketris MP (2002) *Inorganic matter of coal*. 422 pp. Ekaterinburg, Russia: Ural Division of Russian Academy of Science (in Russian).
- Yudovich YE, Ketris MP (2015) *Geochemistry of Coal. Occurrences and Environmental Impacts of Trace Elements*, chapter 3. In: *Coal Production and Processing Technology*. CRC Press, Boca Raton, pp. 48–73.
- Zhang YY, Nakano J, Liu LL, Wang XD, Zhang ZT (2015) Trace element partitioning behavior of coal gangue-fired CFB plant: Experimental and equilibrium calculation. *Environ Sci Pollut Res* 22(20):15469–15478. <https://doi.org/10.1007/s11356-015-4738-6>
- Zhao Y, Zhang J, Chou CL, Li Y, Wang Z, Ge Y, Zheng C (2008) Trace element emissions from spontaneous combustion of gob piles in coal mines, Shanxi China. *Int J Coal Geol* 73(1):52–62. <https://doi.org/10.1016/j.coal.2007.07.007>
- Zhou C, Liu G, Yan Z, Fang T, Wang R (2012) Transformation behavior of mineral composition and trace elements during coal gangue combustion. *Fuel* 97:644–650. <https://doi.org/10.1016/j.fuel.2012.02.027>
- Zhou C, Liu G, Dun W, Ting F, Wang R, Xiang F (2014) Mobility behavior and environmental implications of trace elements associated with coal gangue: a case study at the Huainan Coalfield in China. *Chemosphere* 95:193–199. <https://doi.org/10.1016/j.chemosphere.2013.08.065>