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## THE EFFECT OF SALINE MINE WATERS DISCHARGE FROM HARD COAL MINE ON THE ECOLOGICAL STATE OF THE VISTULA RIVER

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The aim of the study was to determine the influence of coal mine waters on water quality in the Vistula River. Water samples for laboratory analysis were collected in 2011 and 2012 on one kilometer long section of the river. Basic parameters were measured at the collection spot. The study assesses the dynamics of physicochemical water properties, fulfillment of the quality requirements necessary to introduce contaminated water into the river, water salinity, quality, and utility values. The study indicates that water quality of the Vistula River has been rapidly decreasing as a result of coal mine water introduction. Water becomes degraded, unfavourable for fish communities and unsuitable for use by people. Coal mine water contamination exceeds allowable pollution levels stated by legal regulations. Self-purification of the river is efficient as contamination levels decrease at the length of the examined section of the river.

**Keywords:** water quality, mine water, Vistula River

Extraction of hard coal deposits from the mines in the Upper Silesia Coal Basin inevitably entails pushing up to the surface a considerable amount of underground water, whose presence results from horizontal and vertical hydrogeochemical zonation in the area of this coal basin. Mineralization of these waters increases with deepening of the deposit exploitation at simultaneous decreasing of inflows (Chaber and Krogulski, 1998; Falta, 2003; Paczyński and Sadurski, 2007). Mine waters, beside natural inflow, contain also technological waters, which are supplied to a mine (usually supplied with hydraulic filling) (Pluta, 2005; Pluta and Dulewski, 2006). Natural mine waters contain substances causing pollution of the aquatic environment (Aleksander-Kwaterczak et al., 2010; Dulewski et al., 2010). Of the thirty indices examined in an assessment of mine waters, nine have been identified in the inflows to the mines in The Upper Silesia Coal Basin: ammonium nitrogen, sodium, iron, potassium, chlorides, sulphates, barium, boron and pH. The contents of the above mentioned indices have been exceeded many times, in which sodium, chlorides and barium between several hundred to even a thousand times (Helios-Rybicka and Rybicki, 2003; Rózkowski and Przewłocki, 1974). In most cases, mine waters are discharged directly or indirectly through settling tanks to rivers. It increases the flow rate and contributes to degradation of water quality due to strong salinification (Helios-Rybicka and Rybicki, 2003). Arduousness of mine waters is evidenced as the load of pollutants supplied to the environment, whereas total chloride and sulphate content is crucial. Increased load of chlorides and sulphates was noted by hard coal mines over the last decade, until 2007. At that time, their load reached a maximum of 4,183.2 t d<sup>-1</sup>. A salt load of 3,496.9 t d<sup>-1</sup> was discharged to surface waters in 2008, of which 2/3 entered the Vistula River catchment (Chaber and Krogulski, 1998). The consequences of water salinification in water courses are unfavourable both for the environment itself (direct effect) and for economic activity (direct and indirect effect). In the aquatic environment,

the number of microorganisms responsible for water self-purification is reduced. At the same time, enzymatic activity declines, whereas liquidation activities towards nonresistant microorganisms intensify (intensification of pollution with organic matter). Additionally, excessive water salinification favours river biocenosis and causes corrosion of machinery and appliances which are in contact with saline water. Losses resulting from diminished saline water usability for agriculture and forestry are also evident. Mines strive to diminish the load of supplied pollutants by means of mining and geological methods limiting inflow of saline waters from underground workings and the methods reducing the discharge of saline waters (Chaber and Krogulski, 1998; Pluta, 2005; Pluta and Dulewski, 2006). The aim of the paper is an assessment of the effect of hard coal mine on water quality of analyzed section of the Vistula River on the basis of selected physicochemical indices. Moreover, the quality and usable values of water from the researched river section were determined.

### Material and methods

“Silesia” Mining Enterprise is located in the south-eastern part of the Śląskie province. It is the property of a Czech group operating in the energy and industrial sector (Energetický a průmyslový holding a. s.) The company’s activity involves mainly hard coal extraction. Mine waters generated by the mine operation are discharged to a storage and dosing reservoir from which they find their way to the Vistula river by the Biała river mouth (Falta, 2003). Field research was conducted in 2011 and 2012. Water samples for analyses were collected at random in measurement-control points located along the analyzed Vistula river section: 20 m upstream of the discharge (1) at the outlet – at the river kilometer 33.08 (2), 50 m (3) and 1000 m downstream of the mine water outlet – 4 (Figure 1).



Figure 1 Location of measurement-control points

Water temperature using CO-411 oxygen meter, dissolved oxygen and water oxygen saturation, water pH by CP-104 pehameter, and electrolytic conductivity (EC) with CC-102 conductometer were measured directly on site. The following assessments were conducted in the laboratory of the Department of Land Reclamation and Environmental

Development, University of Agriculture in Krakow: total suspended solids (ZO) were determined using gravimetric method, dissolved solids (SR) by evaporating, ion concentrations of calcium (Ca<sup>2+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), magnesium (Mg<sup>2+</sup>), manganese (Mn<sup>2+</sup>) and total iron (Fe<sub>og</sub>) were assessed using atomic absorption spectrometry on UNICAM SOLAR

969 spectrometer. Concentrations of ammonium (N-NH<sub>4</sub><sup>+</sup>), nitrite (N-NO<sub>2</sub><sup>-</sup>) and nitrate (N-NO<sub>3</sub><sup>-</sup>) nitrogen and total phosphorus (P<sub>og</sub>), phosphates (PO<sub>4</sub><sup>3-</sup>) and chlorides (Cl<sup>-</sup>) were assessed by means of colorimetric flow-injection analysis on FIAstar 5000 apparatus. Concentrations of sulphates (SO<sub>4</sub><sup>2-</sup>) were determined using precipitation method, whereas NO<sub>2</sub><sup>-</sup> concentration was calculated from the results of N-NO<sub>2</sub> assessments. Physicochemical indices were determined once a month (Rozporządzenie Ministra Środowiska z dnia 4 października 2011...).

### Results

According to the regulation of 2006 (Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006...), values of three indices, ammonium and nitrite nitrogen and total phosphorus, were exceeded. Concentration of ammonium nitrogen ranged from 4.25 to 30.1 mg dm<sup>-3</sup> – i.e. was thrice higher than the permissible

Table 1 Range and mean values of physicochemical features of water of the Vistula River in four measurement-control points and the evaluation of mine water (point 2)\*

Specification	Permissible value**	Range Mean		Sewage supplied to water	
		2	4	2	4
Temperature in °C	35	5.4–18.8	5.1–17.3	N	–
		13.08	11.59		
pH	6.5–9	6.55–7.41	6.32–7.63	N	–
		7.11	7.27		
Total suspended solids	35	1–26	0.6–5.5	N	–
		12.6	2.5		
N-NH <sub>4</sub> <sup>+</sup>	10	4.25–30.1	0–1.59	T	–
		14.48	0.48		
N-NO <sub>3</sub> <sup>-</sup>	30	0.94–2.99	0.4–2.8	N	–
		1.87	1.4		
N-NO <sub>2</sub> <sup>-</sup>	1	0.07–1.27	0.09–0.30	T	–
		0.36	0.16		
P <sub>og</sub>	3	0.02–61.74	0.00–0.61	T	–
		12.65	0.14		
Cl <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup>	≤1 000	165.2–33085.6	49.10–340.50	–	N
		19588.7	193.14		
Fe <sub>og</sub>	10	0.11–1.18	0.6–1.68	N	–
		0.61	0.98		

N – non-exceeded value, T – value exceeded according to the regulation of 2006 (Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006...)

Source: \*Rajda and Kanownik, 2007; \*\*Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006...

value according to the regulation in force. Nitrite nitrogen concentration exceeded the permissible value (1 mg dm<sup>-3</sup>). Total phosphorus concentration considerably exceeded its permissible value (31 mg dm<sup>-3</sup>) and ranged from 0.02 to 61.74 mg dm<sup>-3</sup> (Table 1). With respect to the temperature, a majority of analyzed samples classify Vistula river water on the analyzed section to 1<sup>st</sup> quality class (Table 2). Along the investigated Vistula river stretch, water pH ranged from 6.54 to 7.69, i.e. was in the 1<sup>st</sup> class. In the upper course, value of electrolytic conductivity did not exceed 1 000 µS cm<sup>-1</sup> – value admissible for 1<sup>st</sup> quality class (Lipiński, 1987). In

points 3 and 4, concentrations were higher than the values permissible for the 2<sup>nd</sup> quality class, therefore the waters were classified as below the good state according to the regulation in force. Degree of water oxygen saturation along the whole analyzed river length was even and classified it to the 1<sup>st</sup> quality class. On the other hand, dissolved oxygen concentration in measuring-control point 1 was below 7 mg dm<sup>-3</sup>, which ranked the analyzed water to the 2<sup>nd</sup> quality class. Concentrations of dissolved solids matched the 1<sup>st</sup> quality class only in point 1, in the other points, the concentration exceeded the value admissible for the 2<sup>nd</sup>

**Table 2** Range and mean values of physicochemical features of water of the Vistula River and the evaluation of its usability\*, \*\*

Specification		Range			Mean			Quality class***			Water usability for											
											supply to people*				fish habitat**							
											salmonids		cyprinids									
		measurement-control points																				
		1	3	4	1	3	4	1	3	4	1	3	4	1	3	4						
Temperature in °C		4.9–18.2 12.19	5.2–17.4 11.5	5.1–17.3 11.6	I	I	I	A1			yes											
pH		6.54–7.76 7.29	6.66–7.69 7.42	6.32–7.63 7.27	I	I	I	A1		A2	yes											
EC	mS cm <sup>-1</sup>	202–561 282	365–5140 2055	202–2540 831	I			A1	no		-	-	-	-	-	-						
O <sub>2</sub>	%	70–97 85	69–107 93	79–109 94	I	I	I	A1	A2	A1	-	-	-	-	-	-						
O <sub>2</sub>		6.4–9.5 8.2	7.2–11.2 9.3	7.6–13.1 9.2	II	I	I	-	-	-	no	yes	no	yes								
Dissolved solids		68–382 176	280–11734 2465	132–1678 664	I			-	-	-	-	-	-	-	-	-						
Total suspended solids		0.8–7 2.5	0.8–10 4	0.6–5.5 2.5	I	I	I	A1			yes											
N-NH <sub>4</sub> <sup>+</sup>		0–1.13 0.33	0.39–1.59 0.86	0–1.59 0.48	II			-	-	-	yes	no	yes	no								
N-NO <sub>3</sub> <sup>-</sup>		0.2–3 1	0.9–2.8 1.9	0.4–2.8 1.4	II	II	II	-	-	-	-	-	-	-	-	-						
NO <sub>2</sub> <sup>-</sup>		0.04–0.26 0.11	0.10–0.39 0.22	0.09–0.30 0.16	-	-	-	-	-	-	no											
PO <sub>4</sub> <sup>3-</sup>		0–0.78 0.18	0.00–5.12 1.12	0.00–1.86 0.43	-	-	-	no			-	-	-	-	-	-						
Total phosphorus	mg dm <sup>-3</sup>	0–0.25 0.06	0.00–1.67 0.32	0.00–0.61 0.14	II			-	-	-	no		yes	no								
SO <sub>4</sub> <sup>2-</sup>		16–39 27	26–49 38	17–51 32	I	I	I	A1			-	-	-	-	-	-						
Fe <sub>og</sub>		0.67–2.31 1.15	0.09–1.61 1	0.6–1.68 0.98	-	-	-	no	A2	A2	-	-	-	-	-	-						
Mn <sup>2+</sup>		0.09–0.46 0.21	0.11–0.47 0.24	0.12–0.47 0.21	-	-	-	A3			-	-	-	-	-	-						
Ca <sup>2+</sup>		26–50 34	41–194 97	35–100 55	I	II	I	-	-	-	-	-	-	-	-	-						
Mg <sup>2+</sup>		3.5–8.5 5.0	4.9–65.1 29.6	4.2–42.2 16.3	I	II	I	-	-	-	-	-	-	-	-	-						
Cl <sup>-</sup>		16–109 41	43–1199 675	289–289 161	I		II	A1	no		-	-	-	-	-	-						

Source: \* Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008..., \*\* Rozporządzenie Ministra Środowiska z dnia 27 listopada 2002..., \*\*\* Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006...

quality class and was determined as below the good state. On the other hand, concentrations of total suspended solids and sulphates caused that the waters were classified to the 1<sup>st</sup> class. In compliance with the regulation in force (Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008...), ammonium nitrogen and total phosphorus content classified the upper course Vistula river waters to the 2<sup>nd</sup> quality class, while in its lower course to the state below good. Nitrate nitrogen concentration was even, waters in all points were in the 2<sup>nd</sup> quality class. Assessment of water along the investigated Vistula river section on the basis of mineral values (magnesium and calcium) revealed that values admissible for the 1<sup>st</sup> water quality class were exceeded in point 3 (Table 2). Chloride concentration in point 3 ranged from 43 to 1199 mg dm<sup>-3</sup>, which caused that the Vistula river waters classified below the good state. In compliance with the regulation on water usability for supply to people, four out of 10 analyzed indices (electrolytic conductivity and Cl<sup>-</sup> in points 3 and 4, PO<sub>4</sub><sup>3-</sup> in all analyzed points, Fe<sub>og</sub> in point 1) did not satisfy the requirements for the categories mentioned in the regulation of 2002 (Rozporządzenie Ministra Środowiska z dnia 27 listopada 2002) (Table 2). Waters in all measurement-control points were classified to A3 category due to manganese concentrations and to A2 category because of total iron concentrations (points 3 and 4) and water oxygen saturation (point 3). Water pH only in point 4 included it to A2 category. Values of the other indices were in A1 category. Summing up, even if necessary, water from the analyzed Vistula river section cannot be used for water supply to people. Quality of the Vistula river water does not meet the habitat requirements for the salmonid or cyprinid fish, because according to the regulation in force (Rozporządzenie Ministra Środowiska z dnia 4 października 2002...), nitrite concentration exceeded values permissible for both fish species in all analyzed points (Table 2). For the salmonid fish, in point 1 values of four out of seven indices in the Vistula river waters (the temperature, pH, total suspended solids, ammonium nitrogen) meet the standard, similar as in point 3 (water temperature, pH, dissolved oxygen, total suspended solids), whereas in point 4 only three values meet the standards. On the other hand, for the cyprinid fish in point 1, six indices allow the water on the investigated river stretch to be their habitat, while in points 3 and 4 – four indices.

### Conclusion

Mine waters originating from PG "Silesia" mine draining contain components causing their pollution: ammonium nitrogen, total iron, chlorides and sulphates. Unfortunately, their effect on surface waters has been registered for many years (Lipiński, 1987). Discharge of saline waters is under control, it is dosed depending on the water states in the receiving water using a storage reservoir (settlement tank). Also, the quality of mine waters accumulated in the reservoir and the background of receiving waters are analyzed prior to the discharge. The Vistula river bed along the analyzed section is neither reinforced nor considerably changed in result of anthropogenic activity. Urbanization of the adjoining area is slight; the land is used mainly for meadows and arable fields. The terrain along the bed is covered by rich riparian vegetation shading the watercourse. All these

factors allow for the reduction of pollutants supplied by the mine on a satisfactory level (Falta, 2003; Sobolewski, 1992). Mine waters, treated as sewage and infused to surface waters, do not meet the requirements stated in the Regulation of the Minister of Environment dated 24 July 2006 on conditions to be met when discharging sewage to waters or to the soil and on substances of particular adverse impact on the water environment (Journal of Laws, 2006). Permissible values of ammonium and nitrite nitrogen, and total phosphorus were many times exceeded. Limit value of total content of chlorides and phosphates in place of total mixing of saline waters with receiving waters (point 4) is much lower than permissible. Water quality and resulting usable values change along the watercourse with changing anthropogenic pressure in the catchment area (Aleksander-Kwaterczak, et al., 2010; Dulewski et al., 2010; Kanownik et al., 2011). Counteracting the pollution usually accomplished through sanitation of the settlement areas, comprising construction of sewerage system, efficiently operating sewage treatment plants (Kanownik et al., 2013; Policht-Latawiec, 2012; Rajda and Kanownik, 2007) and precipitation water treatment plants, under specific conditions may be supported by the self-cleaning process, which is one of more important features of flowing waters (Bogdał, Kanownik and Wiśnios, 2012; Kanownik and Rajda, 2011).

Analysis of the research results revealed that in the initial section, in point 1, water had the best quality – in 2<sup>nd</sup> quality class, while in point 3, i. e. 50 m downstream of the mine water discharge was the worst due to its electrolytic conductivity, concentrations of dissolved solids, ammonium nitrogen, total phosphorus and chlorides, which exceeded the concentrations permissible for the 2<sup>nd</sup> water quality class, therefore the waters were determined as below the good state. The other indices classified water to the 1<sup>st</sup> quality class, except for nitrate nitrogen, magnesium and calcium (2<sup>nd</sup> class) (Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008...). Analyses of usable values of the Vistula river water demonstrated that it cannot be used for supply to people because of high concentration of phosphates (Rozporządzenie Ministra Środowiska z dnia 27 listopada 2002...). The Vistula river does not satisfy the requirements for natural fish habitat because of dissolved oxygen (points 1 and 4), ammonium nitrogen (points 3 and 4), nitrites and phosphorus in case of salmonid fish, whereas meets the requirements for the temperature, pH, total suspended solids in all points, dissolved oxygen in point 3, and ammonium nitrogen in point 1. Considering the cyprinid fish, the Vistula water may provide habitat due to four indices: the temperature, pH, dissolved oxygen and total suspended solids, and ammonium nitrogen and total phosphorus only in point 1. The other analyzed indices did not satisfy the requirements posed in the regulation in force (Rozporządzenie Ministra Środowiska z dnia 4 października 2002...). Water quality worsens at saline water discharge to the Vistula river which is reclassified from the 2<sup>nd</sup> quality class to water below the good state. However, the content of pollution indices in relation to the mine water discharge point diminishes at the end of the analyzed section. It evidences a good self-cleaning of the water in the river.



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