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Monitoring and Quality Assessment of Selected Physical and Chemical Parameters of the Sola River System, South Poland

1. Introduction

In the Earth's wheel of life, rivers provide the balance. They serve as constant carriers of water and nutrients to areas all around the globe, provide habitat, and mean of transport, with the use of their power, much electrical energy is generated, they leave valuable deposits of sediments, and they provide employment, and recreation as well as other cultural activities.

Despite being the most important freshwater source for man, for centuries rivers have been used as a dumping ground for all sorts of waste, without any control over it. However, waste may be diluted or carried away by current, but certainly will never disappear. Although rivers have a great potential to brake down some of the introduced waste material, such as plant and animal waste, the quantities discarded by today's society result in overloading, called pollution, which disrupts the equilibrium of the river ecosystem.

Over the previous decades, pollution has been inseparable from the development. Together with rapid changes in the industrial sector and technology advancement, we were also facing the increasing pollution of river systems. In response, as to prevent possible future catastrophes and abate water pollution, governments enacted legislation regulating the maximum level of contaminant introduced to the freshwater body. Standards limit concentrations of chemicals to the levels that do not produce harmful effects, and set ranges of physical and biological parameters so that to maintain equilibrium in the ecosystem.

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The objectives of the Sola River studies was to:

— investigate the selected physical parameters (temperature, dissolved oxygen, pH, and conductivity) in the river water;
— to establish the spatial variability in concentrations of metals (Pb, Zn, Cd, Tl, Cr, Ni, As, Fe) for river water, suspended matter and bottom sediments along the Sola River course;
— to assess the scope of potential contamination in the Sola River system by
— comparison with the polish surface water quality classes, LAWA classification system for suspended matter, and Igeo classification for bottom sediment pollution;
— to evaluate the influence of the Sola River system on the Vistula River;
— to estimate the mobility of elements in suspended matter and bottom sediments.

2. Site Characterization

Situated in the south Poland, the Sola River is the biggest river in Beskid Zywiecki mountain range. This 89 km long river has a mean discharge at its mouth of 19.3 m^3/s, and catchment area covering approximately 1391 km^2 [7]. The Sola River is the first right tributary of the Vistula River, with which it merges in the region of Oswiecim. In the vicinity of the upper Sola River forests and agro-pastoral economy prevails. Small and medium size farms are dominated mainly by cattle and sheep breeding, as well as crops, vegetable and fruit cultivation. There are three main industrial centers located in Oswiecim – chemical industry, in Kety – the nonferrous industry, and in Zywiec – associated with brewery. Each of those industrial centers has its own waste disposal facility and sewage treatment plant.

In order to protect the region from frequent flooding, as well as to equalize the discharge of upper Vistula River, the Sola River had been managed by building three water storage reservoirs:

1) in Tresna – Zywieckie Lake,
2) in Porabka – Miedzybrodzkie Lake,
3) in Czaniec.

3. Sampling and Methods

A study was initiated in 2001 to monitor the river water quality including the suspended particulate matter (SPM) and bottom sediment along the Sola River course, on a distance of about 76 km. The samples were taken in the winter 2001 (on December 08) and in the spring 2002 (on April 20), to check for the seasonal changes in selected physical and chemical parameters of the investigated surface water system. River water and SPM were monitored in both of the sampling seasons, whereas bottom sediment samples were collected only during the winter.

Location of the sampling points was chosen in order to assess the potential impact of industry, agriculture, sewage treatment plants, landfills as well as urban areas, on the Sola River system quality. The samples were collected form 12 sampling points, from which 10 were set on the Sola River and additional 2 on the Vistula River, the purpose of which was to investigate the influence of the Sola River on the Vistula River contamination (see Fig. 1, Tab. 1).

River water samples were collected using a hand pump and filtrated through a 0.45 μm membrane filter into two 50 ml flasks. One of those flasks was acidified with HNO_3 for further ICP-MS analysis, and the second was used for anion analysis on IC apparatus. River water parameters such as: pH, dissolved oxygen, temperature and conductivity were measured in the field.

The concentration of SPM was measured. Samples taken in the winter season from sampling points: 4 to 6, as well as samples taken in the spring season form sampling point 2 to 10 were excluded from further analysis because of high analytical error associated with negligible mass of residue accumulated on the filter. Dried filters with accumulated SPM followed Aqua Regia digestion procedure and further ICP-MS and AAS analysis took place.

Bottom Sediment samples were collected in winter seasons from points 1, 2, 3, 10 on the Sola River and point 12 on the Vistula River. In the laboratory were separated according to fraction content using 63 μm sieve, and obtained fractions (< 63 μm and > 63 μm) were dried for 10 hours period. Clay and silt fraction followed microwave digestion (Aqua Regia). Further determination of element concentrations using ICP-MS and AAS took place.

Suspended matter leaching test was performed on samples: 1-Rajcza, 11-Babice, and 12-Bobrek, whereas the bottom sediment leaching included preparation of samples: 1-Rajcza, 3-Zywiec, 10-Broszkowice, and 12-Bobrek (see Fig. 1, Tab. 1). To each of investigated samples, an appropriate amount of buffering solution (Na-acetate and acetic acid, at pH 5) was added, in order to keep the sample: solution ratio 1:20 in case of SPM samples, and 1:4 in case of bottom sediment samples [2]. Samples were shaken for 2 hours and further ICP-MS analysis of the obtained solutions was performed.

4. Precision and Accuracy

With respect to accuracy and precision the analytical quality was assured by application of following steps:

— reference materials were analyzed every 7th sample: river water reference material 1643 d, and suspended matter and bottom sediment reference material LSKD 4;
— blank samples were prepared for river water, suspended matter and bottom sediment;
— internal standard Rh^{+} (Rhodium) was used for ICP-MS analysis to minimize interferences of apparatus;
— duplicates of samples were used.

5. Results and Discussion

5.1. River Water Quality

Natural waters are never pure H_2O but a complex and constantly changing mixture of dissolved organic and inorganic substances as well as suspended particles. Viewed from the total amount of dissolved substances in river waters, metals constitute only a small portion, namely: 2.5% Cr, 2.9% Mn, 0.98% Cu, 0.5% Ni, and 0.13% Fe [12]. The anthropogenic changes in river water quality are superimposed on the natural background variations. However, due to the adsorption of trace elements by particulate matter, which occurs at normal pH and redox conditions, the actual dissolved element concentrations introduced to the river waters are very low. Thus, the monitoring of trace elements in river water only does not necessarily reveal the actual contamination of the system.

The temperature values of the Sola River water ranged between 3.5–5°C during the winter, and oscillated around 6°C during the spring. Dissolved oxygen was measured at two sampling points located on the Sola River: point 1 in Rajcza, and point 6 in Kety. During the winter the concentration [mg/l] in Rajcza was 7, whereas during the spring it decreased to the value of 6. Such concentrations are within the first quality class. In Kety the dissolved oxygen levelwas lower: 5 in winter, and 4 in the spring, which is the second and third quality class respectively. In sampling point 12-Bobrek, the Vistula River is out of any quality class, and was at the level of 3 in both of the sampling seasons.

With respect to pH parameter Sola River met the first class quality standards. The values were between 7 and 9 in both of the sampling seasons. The pH of the

Vistula River was lower in comparison with the Sola River pH, and the values were at the level of: 7.29 in Babice, 7.33 in Bobrek during the winter, and 7.22, 7.13 during the spring, in Babice and in Bobrek respectively.

The conductivity values [μS] in the Sola River water were low and oscillated around 0.3. Whereas the conductivity in the Vistula River water was much higher and exceeded the maximum allowable level of any quality class, and was: 4.12 in Babice, 6.04 in Bobrek during the winter, and 6.94, 7.55 during the spring in Babice and Bobrek respectively.

The content [μg/l] of investigated metals (Pb, Fe, As, Zn, Cd, Cr, Tl, Ni) in the Sola River water was very low, in some cases being below ICP-MS detection limit. Such concentrations of metals rank the river within the first purity class in both of the sampling seasons.

The Sola River water showed negligible concentrations of Cl ions [mg/l] which ranged from 4.02 in Porabka to 15.16 in Oswiecim. Elevated concentrations up to 32 were found in the Vistula River water before Sola tributary (point 11-Babice), however the concentration was lower – 11.0 in point 12-Bobrek. With respect to Cl ions content, the Sola River water meets the first class surface water quality criteria.

Concentrations of NO_3 ions [mg/l] in the Sola River showed moderate to high contamination of the river water. The lowest concentrations were found in Rajcza 3.98, and in Porabka 4.27 and those were the only sampling points where water met the first surface water quality criteria of < 5.0 mg/l. River water in points 5 to 7 exceeded this standard, and ranged within the second class. The rest of the water samples revealed high concentrations of NO_3 ions fitting the third quality class: 8.22 in Wieprz, 9.15 in Zywiec, 7.86 in Bielany, 7.26 in Oswiecim, and 7.12 in Broszkowice. The Vistula River water is also contaminated with NO_3 ions carrying considerable concentrations in the range of third quality class: 12 mg/l in Babice, and 11.4 mg/l in Bobrek.

Of no contamination was the Sola River water with respect to SO_4 ions. Concentration values [in mg/l] ranged from 17.5 in Rajcza to 26.8 in Oświecim and the concentrations in the Vistula River were also negligible: 36.0 mg/l in Babice, and 26.9 mg/l in Bobrek. The overall quality of the Sola River water can be classified into first, second and the third polish surface water quality class, with no single sampling point being out of classes (Fig. 1).

It was observed that the Sola River is acting as a dilution media on the Vistula River. The concentrations of investigated elements dropped significantly in sampling point 12 – after Sola River tributary in comparison with the sampling point 11 – before Sola River outlet to the Vistula River.

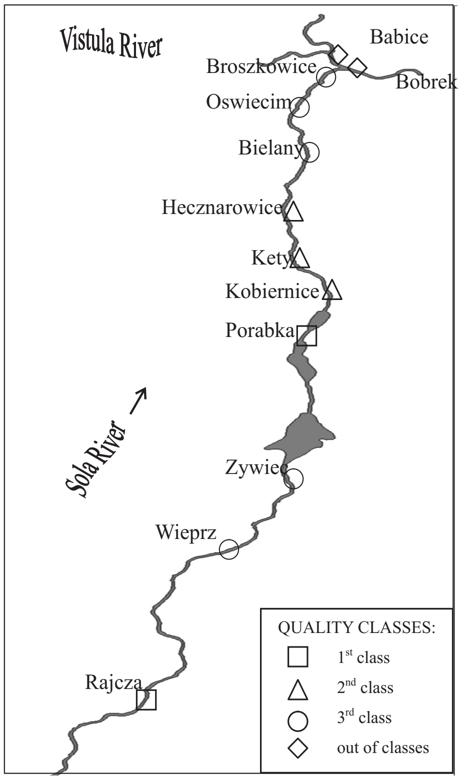

Fig. 1. Quality of the Sola River water with respect to chemical parameters according to Polish Surface Water Quality Classes [8]

5.2. Suspended Particulate Matter (SPM) Quality

A river carries not only the water itself but also material in suspension or as a bed load transported by traction along the bottom. Suspended matter is composed of insoluble particles of soil, sand, silt, clay minerals and organic particles that are greater than 0.45 μm, whereas particles smaller than 0.45 μm are referred to as dissolved matter. Particulates function as a transport vessel for many contaminants, such as heavy metals which while entering the water may be readily adsorbed onto the solid surfaces [4]. The SPM serves as a unique registrar of even smallest fluctuations in the concentration of heavy metals. The specific surface area is a key particle property which controls adsorption capacity. It is inversely proportional to particle size and decreases over three orders of magnitude from clay-sized particles (10 m^2/g) to sand grains (0.01 m^2/g) [10]. The trace element content is directly proportional to the amount of the finest fraction, therefore the finest particles are the richest in trace elements. As such, it is essential that the quantity and origin of SPM in a river are known.

The Sola River is a mountain river and as such, during the periods of low water level, it carries only small amount of SPM. The amount it carries ranges from 0.22 mg/l in Porabka (point 4), to 17.2 mg/l in Zywiec (point 3) during winter season, and from 0.347 mg/l in Kety (point 6) to 5.81 mg/l in Rajcza (point 1), during spring time. Higher amount of SPM was observed during the winter than in the spring season. Concentration of SPM in the Sola River shows three distinct variations that are similar in both of the sampling seasons. The highest concentrations were found in the upper course of the river. In Porabka (point 4) the concentration drastically decreases to the lowest value, and further throughout the middle course, to sampling point 7 in the winter and 8 in the spring, low concentrations prevail. The sudden drop of the load carried is a result of the two dams located on the Sola River. In the lower course of the river, from Bielany (point 8), the Sola River gradually increases the concentration of SPM carried, to the values of 14.6 mg/l near its outlet to the Vistula River in Broszkowice (point 10) during winter, and 1.18 mg/l during spring.

Results of the studies carried out, showed that the concentrations of investigated metals are much higher in SPM in comparison with the river water, which indicates that much of the contamination is readily adsorbed onto the solid surfaces. The detected levels of metal concentrations in SPM were found to exceed the geochemical background values given by Turekian and Wedepohl [11] (Tab. 1).

Table 1. Variability of metal concentrations in suspended matter of the Sola River in comparison with the Vistula River

Sampling point	WINTER (2001 December 08) concentration [mg/kg]							
	Pb	Zn*	Cd	Tl	Cr	Ni	As	Fe
1-RAJCZA	52.5	420	2.41	0.204	72.4	67.2	9.44	30725
2-WIEPRZ	85.7	406	3.69	0.327	87.9	64.5	10.1	35127
3-ZYWIEC	79.8	343	2.36	0.319	70.8	61.3	13.3	34201
7-HECZNAROWICE	19.4	1725	0.86	0.087	68.3	52.5	18.1	22815
8-BIELANY	124	750	5.78	0.474	176	61	23.4	44675
9-OSWIECIM	94.5	419	3.25	0.568	125	63.9	26.8	54007
10-BROSZKOWICE	79.7	354	3.12	0.341	83.2	60.9	32.1	45315
11-BABICE/Vistula	786	3021	31.7	2.73	315	75.1	46.4	64285
12-BOBREK/Vistula	749	2974	29.2	2.57	205	46	38.9	38874
Sampling point	SPRING (2002 April 20) concentration [mg/kg]							
	Pb	Zn	Cd	Tl	Cr	Ni	As	Fe
1-RAJCZA	261	84.1	0.456	0.223	7.37	1.90	b.d.l	1062
11-BABICE/Vistula	934	1188	8.09	1.43	52.8	20.7	17.7	62896
12-BOBREK/Vistula	833	657	3.92	0.893	25.6	13.7	8.45	10402
Background value	20	95	0.3	–	90	68	–	–

* Concentration determined using AAS
b.d.l. – below ICP-MS detection limit

Concentration of elements [in mg/kg] in the Sola River SPM during winter season ranged: Pb 19.4–94.5, Zn 343–1725, Cd 0.86–5.78, Tl 0.087–0.568, Cr 68.3–176, Ni 52.5–67.2, As 9.44–32.1, and Fe 22815–54007. Quality assessment with respect to Pb, Zn, Cd and Ni has been made on the basis of the German LAWA classification system introduced by Irmer [3], and relative highest pollution was found with Cd and Zn (Fig. 2). Table 1 presents variability of metal concentrations in suspended matter of the Sola River in comparison with the Vistula River.

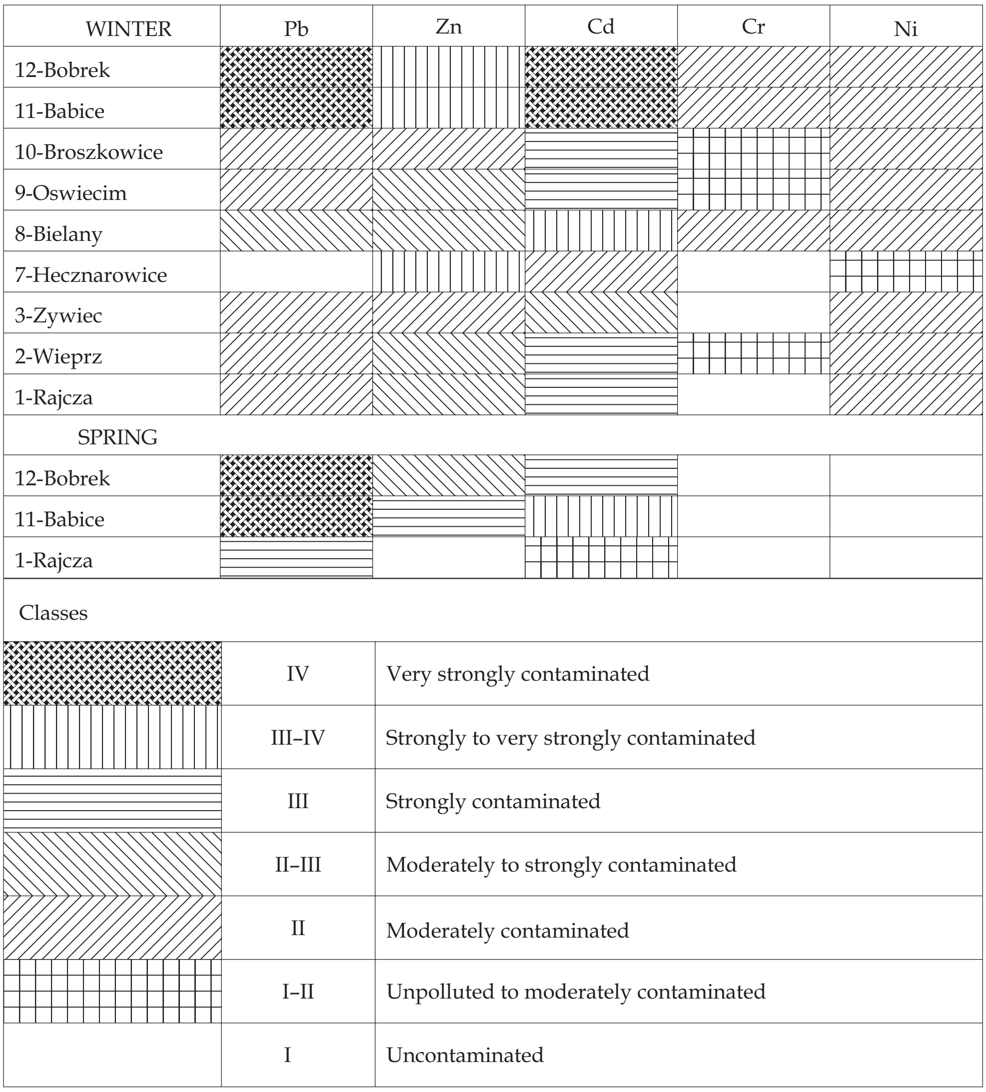

Fig. 2. Suspended Matter Quality according to LAWA classes [3]

5.3. Bottom Sediments Quality

In bottom sediments of a river system, heavy metals are associated mainly with clay minerals, carbonates, silicates and organic substances of anthropogenic origin [9]. However, immobilized in bottom sediments heavy metals do not necessarily stay in that condition, but may be released as a result of chemical changes in aquatic system [1] and also because of turbulence flow. The remobilization processes of the metals from the particles of suspended matter as well as sediments are potentially very hazardous. The establishment of metals pollution level in bottom sediment plays an important role in detecting sources of contamination in river environment, even long after the input has taken place.

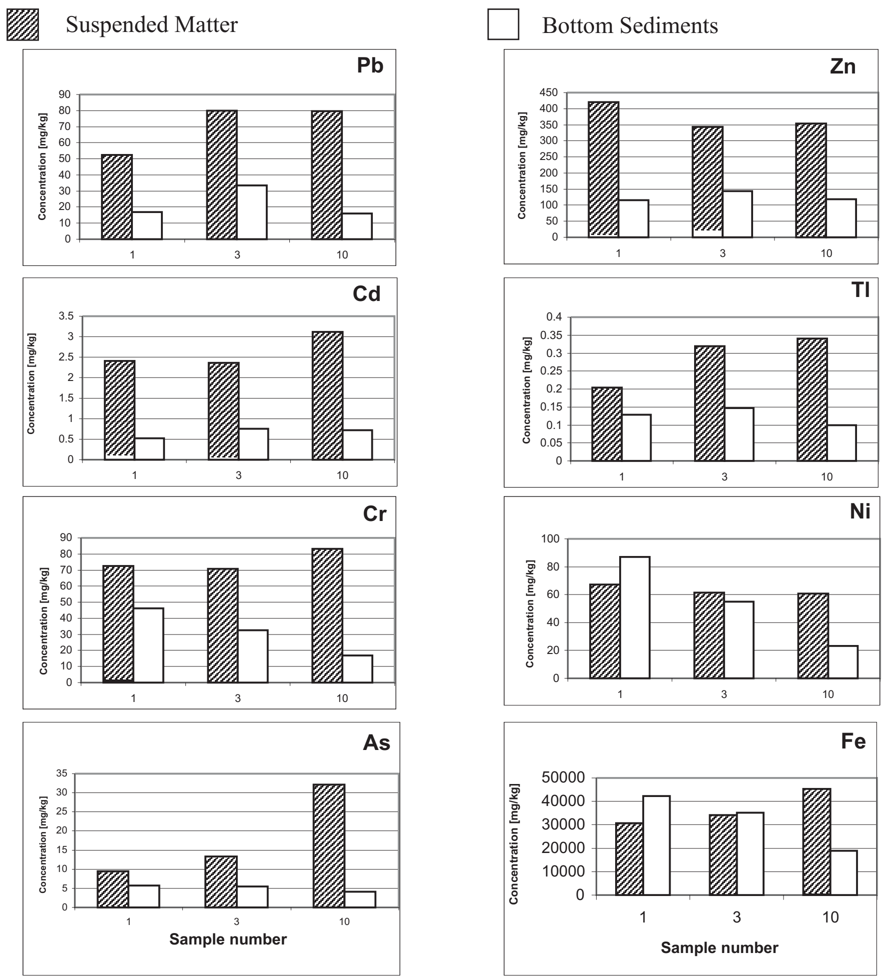

Fig. 3. Comparison of metals content [mg/kg] in suspended matter with bottom sediments

In the Sola River bottom sediment coarse size fraction, above 63 μm, prevails. The grain size fraction below 63 μm does not exceed the concentration of 30%; in Rajcza (point 1) 6.7%, in Wieprz (point 2) 2.4%, in Zywiec (point 3) 29.5% and in Broszkowice (point 10) 18.9%. Sample taken from the Vistula River bottom sediment in point 12-Bobrek, shows the concentration of fraction below 63 μm of 13.9%.

Concentrations of metals in the investigated bottom sediment samples revealed lower contamination levels in comparison with suspended matter (Fig. 3) and ranged [in mg/kg]: Pb 15.9–33.4; Zn 87.4–144; Cd 0.518–0.942; Tl 0.099–0.147; Cr 16.8–32.6; Ni 23.1–54.9; As 4.07–5.72; Fe 18932–42267. Figure 3 shows comparison of metals content [mg/kg] in suspended particulate matter with bottom sediment. Quality assessment of Pb, Zn, Cd, Cr, Ni and Fe contamination has been made on the basis of the I_{geo} classification system introduced by Müller [5]. Generally bottom sediments of both the Sola River and the Vistula River are not contaminated with respect to Cr, Ni and Fe. Concentrations of Pb and Zn in Sola River indicate uncontaminated to moderately contaminated conditions, whereas in the Vistula River strong and very strong contamination. The highest metal contamination in the Sola River bottom sediment is with respect to Cd and was found in upper river course (point 2-Wieprz). Obtained concentration in this very point, indicates the second I_{geo} class, which refers to moderately contaminated conditions (Fig. 4).

The further results of the composition of the Vistula River bottom sediment samples determined using SEM-EDX method shows Figure 5.

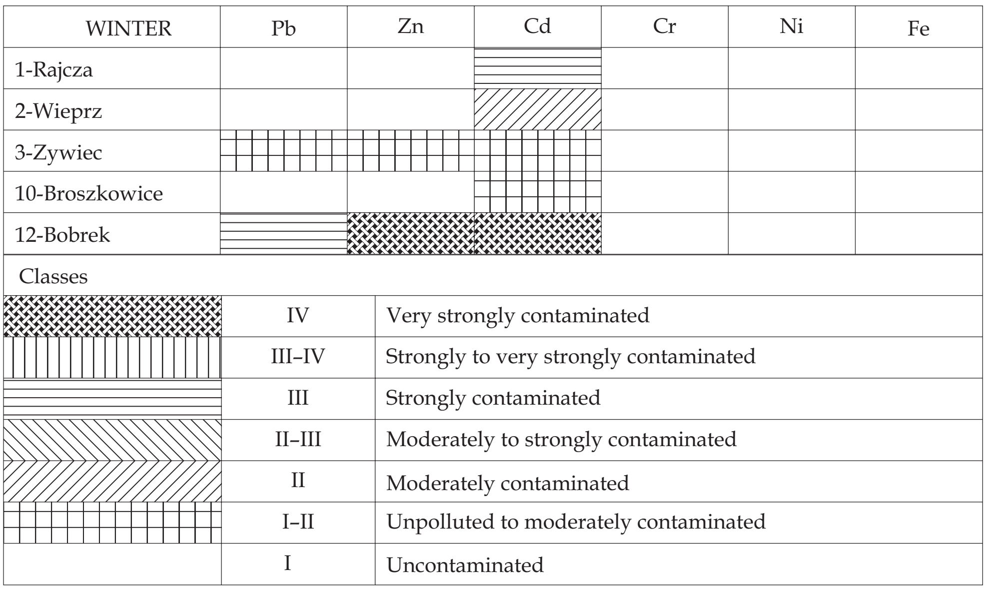

Fig. 4. Bottom Sediment Quality according to I_{geo} classes [5]

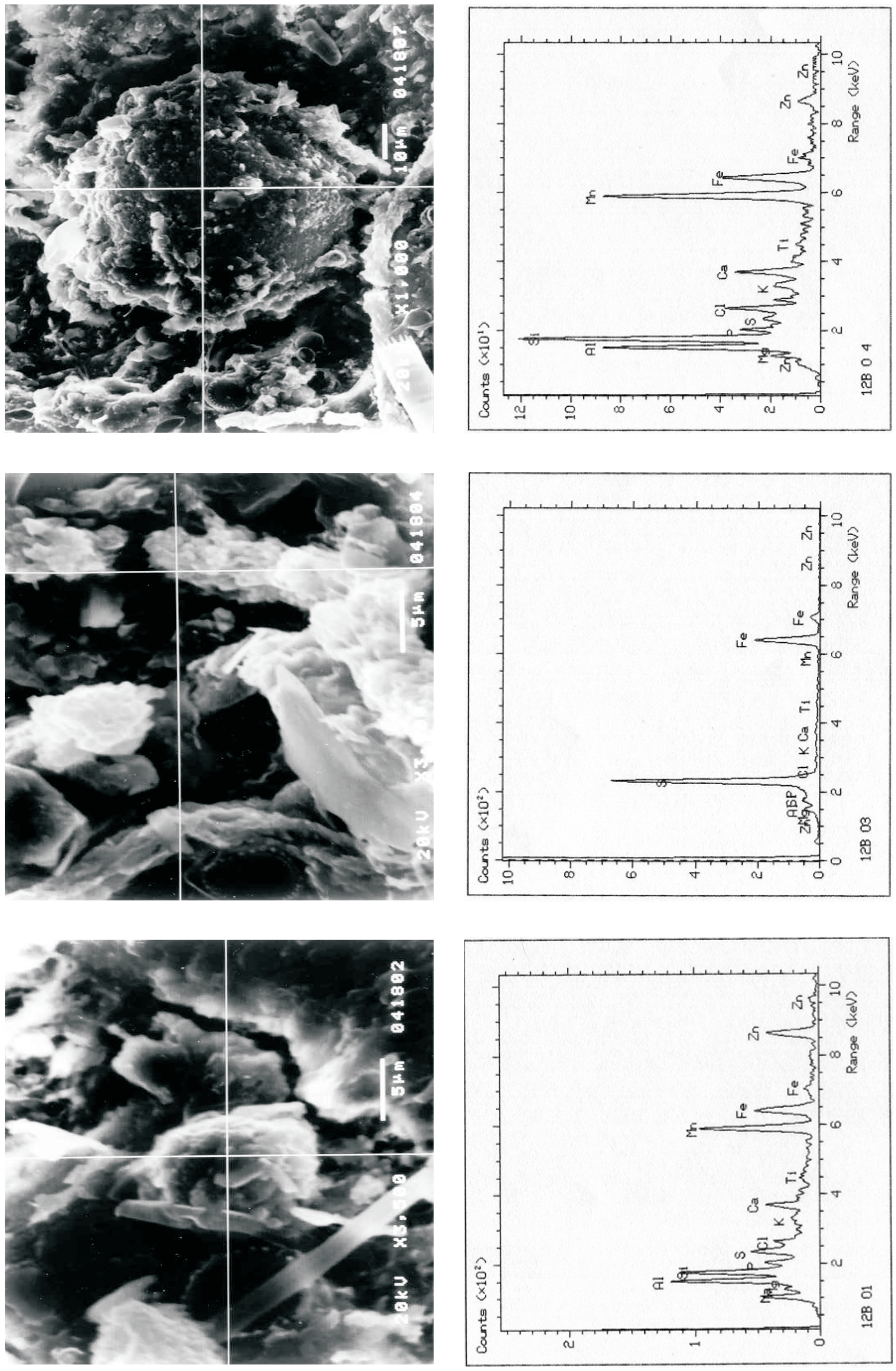

Fig. 5. SEM-EDX results of the Vistula River bottom sediment samples determined

6. Leaching Test

It is widely recognized that the key to understanding the heavy metal behavior and its impact on environment is not only its total concentration, but speciations of the metals. The distributions amongst its chemical forms or species, as well as the reactions involved in transformation of those species are of main importance. Processes, which affect metal speciation in an aquatic environment, are: dilution, adsorption, precipitation/dissolution equilibria and oxidation/reduction reactions [6]. Studies on speciation of heavy metals and its incidence on their mobility lead to conclusion that solid species tend to be less mobile than the colloidal or dissolved forms.

Leaching test was conducted to perform metal mobility in the suspended matter and bottom sediment samples and investigate the amount of metal released in response to weekly acidic environment conditions (see: p. 3, *Sampling and Methods*).

According to the obtained results, most metals contained in the Sola River suspended matter, revealed low leaching capacity. While immobile and not bioavailable, those metals do not pose threat to the environment. Generally, metal leachability in the investigated Sola River samples did not exceed 22%, whereas Pb, and Fe shows the least mobility found to be below ICP-MS detection limit. Only Ni seems to be very mobile metal, till leached out from the suspended matter up to 97%. According to Polish regulations for Maximum Contaminant Level introduced into the ground [8] all metal amounts released from the suspended matter fit the standards.

Bottom sediment leaching results indicate that lowering pH generally promotes metals mobility and bioavailability, thus releasing Pb, Cr and Fe contaminants in portions exceeding Polish standards.

7. Conclusions

Results obtained lead to formulation of following conclusions and further recommendations for national chemical monitoring in Poland:

1. Investigated physical parameters met the 1st and the 2nd polish surface water quality class during the winter and spring respectively. The metal concentrations in the Sola River did not exceed the values of the 1st surface water quality class in both of the sampling seasons. Pollutants content did not reveal significant seasonal variations, therefore chemical monitoring conducted twice a year seems to be sufficient.
2. Metal contamination level was found to be much higher in the suspended particulate matter than in the river waters. Relative highest pollution was observed with respect to Cd and Zn. Results of studies carried out, revealed that the Sola River is acting as a dilution media on the Vistula River.

3. Chemical monitoring of suspended particulate matter should be included in the Polish National Monitoring System on the routine basis. Additional arguments for it are: easy sampling, better homogeneity of material, less time consuming laboratory procedure.
4. Concentrations of metals in the investigated bottom sediments showed lower contamination levels than in suspended particulate matter.
5. Low mobility of metals upon acidic leaching conditions showed that the amount of metals released from suspended particulate matter met the polish standards for maximum pollutant levels introduced into the ground.
6. The primary problem with monitoring and surface water quality assessment is the lack of the uniform worldwide sampling and laboratory procedure and of program. Such, would allow comparing the data and fully investigating the environment quality, especially when dealing with transboundary ecosystems. Most of the countries manage their own monitoring and assessment systems that incorporate different sampling methods and analytical tools, thus informing only about the scope of potential global environment degradation, but not giving the exact, easy to compare information.

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