Zinc Pollution of the Przemsza River and its Tributaries

F. Pistelok*, W. Galas**

* Center of Environmental Research and Survey, Owocowa 8, 40-158 Katowice, Poland

** Department of Analytical Chemistry, Silesian University, Szkolna 9, 40-006 Katowice, Poland

Received 16 April, 1998
Accepted 22 September, 1998

Abstract

This study presents data related to total zinc content in the water of the Przemsza River and its constituents: the Czarna and Biala Przemsza. It determines also the occurrence of dissolved and suspended zinc in selected sections of the tested rivers.

Keywords: zinc, surface waters, waste water, Przemsza Basin, ICP-AES

Introduction

The Przemsza River and its tributaries play a major role in water and waste water management in the Katowice region. A significant load of pollution is discharged **into** these water-courses in the industrial and municipal wastewater disposed from the cities located in the eastern part of the region. According to data from the Center of Environmental Research and Survey, approximately 10.9 m^3/s of polluted water (including approximately 2.74 m^3/s of municipal waste) was generated in 1995 in the total Przemsza River basin. Similar results were obtained from tests performed by the Institute of Meteorology and Water Management in the 1980s. The percentage of water from different sources in the flow in the testing section in Jelen was estimated to be 46-49% [1,2].

Industry developed in the basin of this river is unique as it resulted from the natural resources that occur in the region, namely coal and non-ferrous metal ores. Major amounts of zinc in brine and industrial wastewater from mining and steel plants are discharged to the water and streams that flow through the area.

Municipal waste water and storm water is also a significant source of zinc. In the former case, zinc is rinsed out from zinc-coated pipes that have been a major component of water supply pipelines for many years. In the latter case, soil contaminated with zinc and mining and non-ferrous smelting waste landfills are in charge of its presence [3, 4].

The objective of this study is to present data related to zinc pollution of the Przemsza River and its tributaries. The described tests involve the ICP-AES technique. This technique seems to be very useful in the case of water analysis. The findings presented in this study are follow-ups of previous work on analytical application of ICP-AES for determining metals in surface water [5].

Methodology of Research

Description of Tests

This study presents findings of total zinc analysis in the tested sections within the scope of the regional monitoring of flowing surface waters, located on the Przemsza River and its major tributaries - the Biala and Czarna Przemsza obtained in 1994 and 1996. Additionally, it presents data related **to** zinc content in the Vistula River in the sections located in Nowy Bieruri and Bobrek (Fig. 1). Afterwards, average, minimum and maximum concentrations (as well as a so called guarantee concentration) were determined in **the** series of 12 or 24 results with 90% probability calculated in compliance with Nesmerak's formula.

Moreover, additional analyses were performed for selected points, the objective of which was to identify zinc forms (dissolved and undissolved) and percentage contents of zinc in suspension.

Experiments

Reagents

Redistilled water, concentrated nitric acid (V) and hydrogen peroxide (30%). All chemicals were of analytical

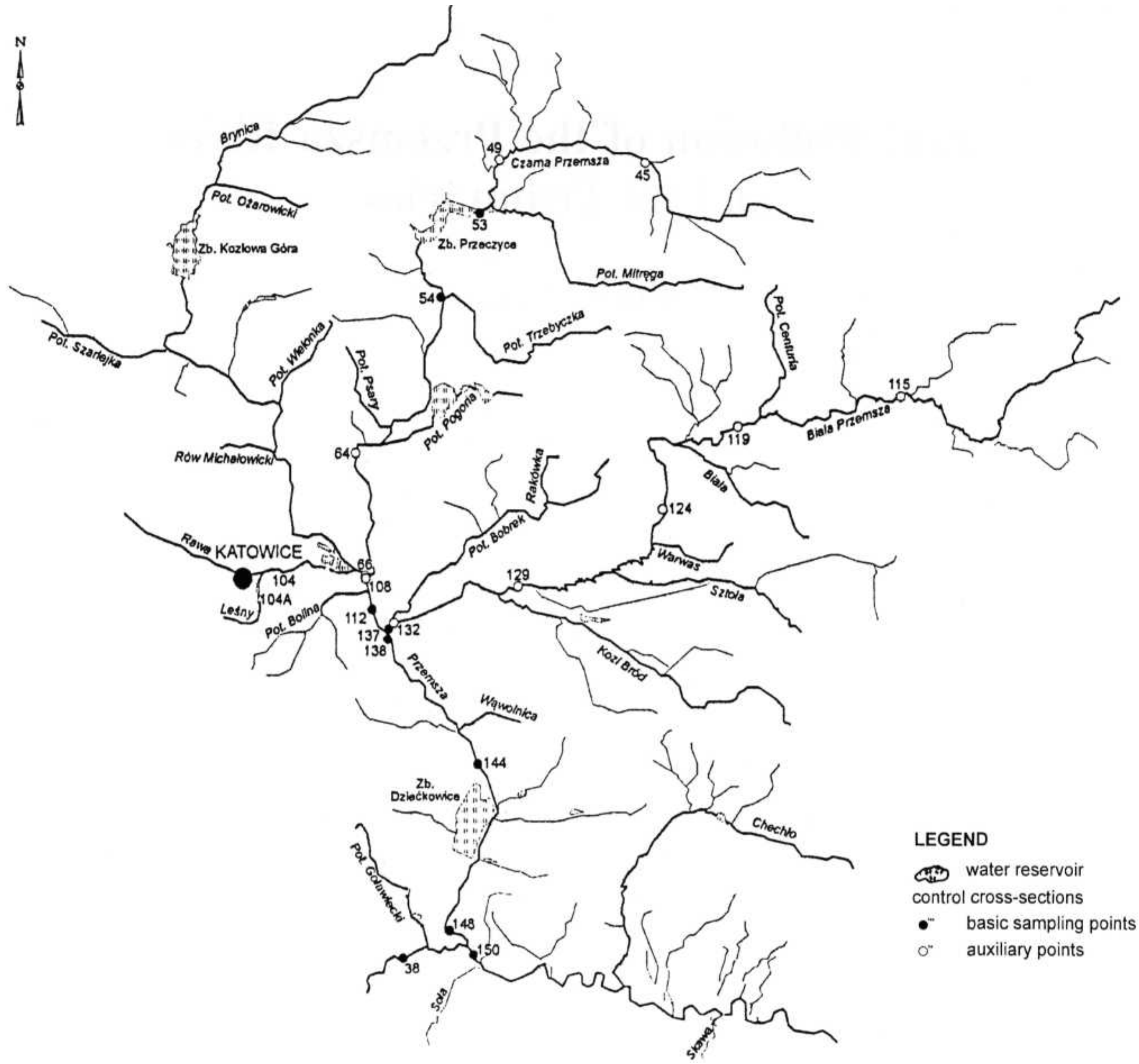

Fig. 1. Hydrographic grid including control and measurement sections in the Vistula, Przemsza, Biala Przemsza and Czarna Przemsza rivers basins.

pure quality. The Merck Zn (II) solution at a concentration of 1 mg/ml was used as a basic solution to make a reference curve.

Apparatus

The Prolabo Rhone-Poulenc MAXIDIGEST MX 350 microwave mineralizer, JOBIN-YVON JY 50P emission spectrometer with excitation in argon inductively-coupled plasma (frequency - 40.68 MHz; power - 1.0 kW; torch - quartz, demountable; plasma gas - 13.0 1/min; sheath gas - 0.2 1/min; carrier gas - 0.3 ml/min; nebulizer - concentric Meinhard, nebulizer pressure - 3.25 bar; spray chamber - glass, according to Scott; sample rate - 1 ml/min; holographic grating - 3600 grooves/mm; wavelength range of polychromator 165-770 nm; integration time - 5s; Zn analytical line - 213.856 nm).

Preparation of Samples

Within the frame of regional monitoring, the analyses were made once or twice a month. 50 ml of a well-stirred water sample that was then mineralized using 2.5 ml of nitric acid was sampled for the analysis. Several droplets of hydrogen peroxide were added to dyed samples. The sample prepared in this way was then heated until it started to boil and it was kept boiling for some time to vapor 3/4 of its volume, and then cooled down and poured to a 50-ml flask and supplemented with redistilled water.

Zinc content in the dissolved and suspended forms was also determined. In order to do that, 1 1 of well-stirred water was filtered through the Pyrex Millipore funnel on the filter paper weighed in advance at the temperature of 105°C. After having been filtered, the filter paper together with the residue was dried until it reached a solid form at the same temperature. The filter paper and the residue were mineralized with nitric acid in a microwave mineralizer. Then the hydrogen peroxide was gradually added until the solution cleared out; the solution was thickened to several ml and diluted to a constant volume. 50 ml of solution that was mineralized similarly to the samples tested within the scope of a regional monitoring was sampled from the filtrate.

Review of Results

In 1994, all analyzed testing sections indicated the occurrence of high zinc concentrations. Upstream of the Biala Przemsza River, in the section located in Golczowice and Bted6w, average zinc concentration exceeded the standard - 0.20 mg Zn/dm^3 [6] - at a relatively small level. It achieved the values of 0.24 mg Zn/dm^3 and 0.32 mg Zn/dm^3, respectively. The other testing sections clearly indicated the impact of waste water and brine from non-ferrous plants; the value of this ratio increased significantly. It reached the level of approximately 1.30 mg Zn/dm^3 in Stawkow and it exceeded slightly 3.00 mg Zn/dm^3 in Maczki.

Higher values occurred in the case of guarantee concentrations. In Btedow the concentration was 0.63 mg Zn/dm^3, and in the last three sections in this river it clearly exceeded 3.00 mg Zn/dm^3, and the maximum value in the Maczki section was 4.67 mg Zn/dm^3.

The situation was definitely better in 1996. In the two first sections, both the medium and guarantee concentrations were lower or equal to 0.20 mg Zn/dm^3 and complied with a standard; they were within the range of 1.00-2.00 mg Zn/dm^3 in the remaining sections. The only concentration that was higher was reported in Maczki - 2.21 mg Zn/dm^3.

Average zinc concentrations in the Czarna Przemsza River up to the section located in Bedzin were within the range of 0.22-0.34 mg Zn/dm^3, and the guarantee concentration within the range of 0.42-0.69 mg Zn/dm^3 in 1994. The values reported downstream were significantly higher. Average concentrations starting from the Radocha section was within the range of 0.47 to 0.86 mg Zn/dm^3, and the guarantee concentration from 0.94 to 1.59 mg Zn/dm^3.

In 1996, average zinc concentration at the Brynica River estuary was lower than 0.20 mg Zn/dm^3. This limit was not exceeded for guarantee concentrations in the sections located in the retention reservoir in Przeczyce and in Bedzin area. The concentrations in other sections up to the Brynica River estuary were within the range of 0.20-0.40 mg Zn/dm^3. At the point where the Brynica River water is received, the water quality clearly deteriorates. It is characteristic that average (1.02-1.28 mg Zn/dm^3) and guarantee

Table I. Zinc concentrations in the Biata Przemsza, Czarna Przemsza and Vistula Rivers (Bieruri and Bobrek sections) in 1994.

No.	Water-course Name	Number of Testing Point	Name of Testing Point	km	Zinc Concentration in mg/dm^3			
					average	guarantee	minimum	maximum
1	Biała Przemsza	115	Golczowice	46.0	0.24	0.38	0.09	0.44
2		119	Błędów	35.0	0.32	0.63	0.10	0.89
3		124	Sławków	23.7	1.27	1.65	0.96	1.76
4		129	Maczki	10.5	3.06	4.67	1.66	4.95
5		132	Mysłowice	1.9	2.32	3.62	1.51	4.02
6		137	Mysłowice – estuary	0.2	2.29	3.45	1.49	3.97
7	Czarna Przemsza	45	Poręba	50.4	0.34	0.52	0.20	0.64
8		49	Siewierz	41.7	0.32	0.53	0.11	0.53
9		53	Upstream Przeczyce	37.0	0.27	0.42	0.13	0.42
10		54	Downstream Przeczyce	26.0	0.25	0.69	0.04	0.90
11		59	Psary	16.6	0.22	0.50	0.03	0.68
12		64	Będzin	12.0	0.29	0.49	0.10	0.60
13		66	Radocha	4.0	0.47	0.94	0.15	0.96
14		108	Downstream Brynica	3.0	0.86	1.59	0.33	1.95
15		112	Estuary	0.5	0.74	1.18	0.46	1.49
16	Przemsza	138	Downstream the Biała and Czarna Przemsza Connection	22.8	3.15	11.94	0.82	19.70
17		144	Jeleń	13.0	2.29	7.93	0.58	11.20
18		148	Chełmek	0.3	1.71	3.23	0.82	4.37
19	Mała Wisła	38	Bieruń	3.6	0.31	0.55	0.09	0.59
20		150	Bobrek	0.5	1.00	2.10	0.61	2.80

Table 2. Zinc concentrations in the Biala Przemsza, Czarna Przemsza and Vistula Rivers (Bieruń and Bobrek sections) in 1996.

No.	Water-course Name	Number of Testing Point	Name of Testing Point	km	Zinc Concentration in mg/dm³			
					average	guarantee	minimum	maximum
1	Biała	115	Golczowice	46.0	0.09	0.20	0.01	0.20
2	Przemsza	119	Błędów	35.0	0.07	0.13	0.03	0.14
3		124	Sławków	23.7	1.26	1.93	0.73	1.96
4		129	Maczki	10.5	1.27	2.21	0.06	2.34
5		132	Mysłowice	1.9	1.00	1.93	0.13	1.98
6		137	Mysłowice – estuary	0.2	0.92	1.61	0.37	1.75
7	Czarna	45	Poręba	50.4	0.14	0.39	0.05	0.48
8	Przemsza	49	Siewierz	41.7	0.11	0.30	0.04	0.37
9		53	Upstream Przeczyce	37.0	0.09	0.13	0.03	0.14
10		54	Downstream Przeczyce	26.0	0.06	0.11	0.02	0.22
11		59	Psary	16.6	0.01	0.22	0.01	0.39
12		64	Będzin	12.0	0.09	0.17	0.03	0.17
13		66	Radocha	4.0	0.19	0.40	0.06	0.45
14		108	Downstream Brynica	3.0	1.28	2.23	0.57	2.31
15		112	Estuary	0.5	1.02	2.08	0.46	3.59
16	Przemsza	138	Downstream the Biała and Czarna Przemsza Connection	22.8	1.07	1.86	0.60	2.86
17		144	Jeleń	13.0	1.06	2.02	0.46	4.02
18		148	Chełmek	0.3	0.93	1.41	0.40	1.68
19	Mała Wisła	38	Bieruń	3.6	0.13	0.25	0.04	0.39
20		150	Bobrek	0.5	0.83	1.20	0.27	5.59

(2.08-2.23 mg Zn/dm³) concentrations in 1996 were higher that the ones that occurred two years earlier.

Maximum zinc concentrations in the whole basin in question were reported in the Przemsza River at a distance of approximately 1 km from the confluence of the Czarna Przemsza and Biata Przemsza Rivers. In 1994, they reached the value up to 20 mg Zn/dm³. An average value calculated for this section was 3.15 mg Zn/dm³, and the guaranteed one 11.94 mg Zn/dm³. Very high values were reported at the water measuring point in Jelen (average - 2.29 mg Zn/dm³, guarantee - 7.93 mg Zn/dm³) and at the Przemsza River estuary to the Vistula River (average - 1.71 mg Zn/dm³, guarantee - 3.23 mg Zn/dm³). The concentrations that occurred two years later did not differ from the ones reported in the Czarna Przemsza and Biala Przemsza Rivers upstream from the confluence.

Zinc concentrations in the Przemsza River distinctly increased its contents in the Vistula River. Similarly, in the case of the water-courses discussed before, its average and guarantee concentration in the section in Bobrek in 1994 was much higher (average 1.00 mg Zn/dm³, guarantee - 2.10 mg Zn/dm³) than in 1996 (0.83 mg Zn/dm³ and 1.20 mg Zn/dm³, respectively).

The dissolved form in the Przemsza River and its tributaries was 25.6-37.8% of total zinc content. This value should be considered to be relatively low. In comparison, the percentage of dissolved zinc was 52.2% in the Vistula River upstream the Przemsza estuary.

The percentage of zinc in suspended solids is also characteristic. Zinc was only 0.3% in the Vistula River in Nowy Bierun; the sections indicating the pollution resulting from the impact of industry featured much higher value that was on average 1.3-2.1 %, and the highest value exceeded 6%.

Discussion

Zinc concentrations that occur in the Przemsza River and its tributaries are the highest in the country. They are a couple or even several times higher than those indicated in the standards [6]. The natural zinc content in pure water equals approximately 0.01 mg Zn/dm³. The values that occur in the Polish rivers are definitely higher. The zinc concentration in the Vistula River in Cracow is 0.190 mg Zn/dm³ according to the State Environmental Protection Institute (PIOS), and approximately 0.048 mg Zn/dm³ in Warsaw. According to the same reference, the fluctuations in the Czarna and Biaia Przemsza Rivers are within the range of 0.026-2.830 mg Zn/dm³ [4]. The results obtained during this study only partially confirm these data. The average concentration in the Biala Przemsza and Czarna

Table 3. Percentage of dissolved zinc in selected sections.

No	No of Testing Point	Name of Testing Point	Value	Zinc Concentration in mg/dm³			Percentage of Dissolved Zinc Content
				Total	Dissolved	Suspension	
1	112	Czarna Przemsza – estuary	average	1.33	0.39	0.94	26.0%
			min	0.64	0.01	0.45	0.8%
			max	3.59	1.48	2.11	52.2%
2	137	Biała Przemsza – estuary	average	1.27	0.49	0.79	37.8%
			min	0.96	0.21	0.34	20.8%
			max	1.75	0.80	1.10	70.2%
3	138	Przemsza – downstream the connection	average	1.09	0.37	0.72	33.7%
			min	0.69	0.10	0.39	6.9%
			max	1.70	0.94	1.30	55.0%
4	144	Przemsza in Jeleń	average	1.46	0.44	1.01	29.8%
			min	0.79	0.04	0.46	3.6%
			max	4.02	1.06	2.96	57.2%
5	148	Przemsza in Chełmek	average	1.50	0.34	1.17	25.6%
			min	0.75	0.04	0.50	5.1%
			max	5.59	1.15	4.44	44.8%
6	38	Vistula in Nowy Bieruń	average	0.14	0.08	0.07	52.2%
			min	0.07	0.02	0.03	20.6%
			max	0.24	0.17	0.16	82.9%
7	150	Vistula in Bobrek	average	1.14	0.48	0.66	36.4%
			min	0.38	0.01	0.22	1.6%
			max	5.05	2.48	2.61	51.5%

Przemsza Rivers were distinctly higher than the minimum and exceeded 0.10 mg Zn/dm^3 in all points, and they reached the maximum of 20 mg Zn/dm^3 that was close to the results obtained [3].

Reported concentrations depend to a large extent on water inflow. This comment is particularly related to these parts of the river that do not receive wastewater from non-ferrous metal plants. It clearly occurred in the Czarna Przemsza River up to the Radocha section and in stream parts of the Biala Przemsza. It is proven by the comparison of the results obtained in 1994 and 1997. In the former, zinc concentration values were twice or even three times as high exceeding acceptable standards both in the case of average and the guarantee values. In 1996, the situation was much more favorable.

The situation is different in the sections where zinc content depends on industrial waste water. The way of discharging the receiver varies. Sometimes, it is regulated by the pumping station operation. Very high periodical concentrations of pollutants may be expected. This phenomenon occurred during this work and is well represented by the data summarized in Tables 1-2 where average and guarantee concentrations reported in 1996 were higher than those that had occurred two years earlier in some sections.

Presentation of 1994 data was governed by extremely unfavorable hydrological conditions [7]. The drought caused very low water levels and minimum flows in rivers, which had a considerable impact on dissolved compound concentrations. The year 1996 was entirely different in these terms. Low water flows occurred in rivers in winter and in July and August. Significantly higher levels were reported in other seasons, and there was a flood threat in May and August [8].

Appendix 1 to the Ordinance of the Minister of Environmental Protection, Natural Resources and Forestry provides for the uniform standard zinc concentrations for all three water purity classes of 0.20 mg Zn/dm^3 [6]. Such stringent standards result from the possibility of the toxic impact of zinc on water organisms. Solubility is a significant factor that decides to a large extent on its uptake. Presented data indicate that in the case of water loaded with industrial waste water the dissolved form is about 30% of total zinc content. The dissolved form percentage is therefore lower than in the Vistula River upstream the Przemsza River.

Opinions on zinc toxicity to water organisms vary. It depends to a considerable extent on the ion form of zinc occurrence, calcium presence and magnesium, as well as pH of the water. Dissolved zinc toxicity [9] depends on the salt where it is incorporated. Zinc sulfate is considerably more toxic than zinc chloride. It also depends on water hardness. Adverse effects are increased distinctly in soft water.

Table 4. Percentage of zinc in suspension in selected sections.

No of Testing Point	Name of Testing Point	Value	Suspended Zinc mg/dm^3	Suspension mg/dm^3	Percentage of Zinc Content in Suspension
112	Czarna Przemsza – estuary	average	0.94	80.0	1.6%
		min	0.45	40.6	0.3%
		max	2.11	190.0	5.2%
137	Biała Przemsza – estuary	average	0.79	40.6	2.1%
		min	0.34	24.6	0.8%
		max	1.10	55.2	3.5%
138	Przemsza – downstream the connection	average	0.72	54.8	1.3%
		min	0.39	40.6	0.8%
		max	1.30	70.6	1.9%
144	Przemsza in Jeleń	average	1.01	53.9	1.0%
		min	0.46	31.6	0.8%
		max	2.96	87.6	5.1%
148	Przemsza in Chełmek	average	1.17	60.0	1.9%
		min	0.50	36.8	0.7%
		max	4.44	100.4	6.3%
38	Vistula in Nowy Bieruń	average	0.07	28.8	0.3%
		min	0.03	14.8	0.1%
		max	0.16	49.6	0.6%
150	Vistula in Bobrek	average	0.66	53.9	1.4%
		min	0.22	22.0	0.4%
		max	2.61	96.4	6.4%

Zinc is toxic for fish [3] at the level of 0.1 mg Zn/dm^3. The same concentrations inhibits self-purification processes. LC50 of zinc for fish is 0.5-5.0 mg Zn/dm^3. According to some other data, zinc in concentrations exceeding 3.0 mg Zn/dm^3 inhibits aerobic purification process and kills protozoa at the level of 20 mg Zn/dm^3, first of all ciliates [9].

Zinc toxicity to humans is significantly lower. This was a decisive factor for less stringent standards in the case of drinking water - the Ordinance of the Minister of Health and Social Welfare (acceptable concentration - 5.0 mg Zn/dm^3) (10). Standard values included in the regular groundwater quality classification developed by PIOŚ were also very high; the standard for la water purity class (top quality water) is 0.5 mg Zn/dm^3, and 5.0 mg Zn/dm^3 for Ib water purity class (high quality water) [11].

Data related to zinc contents in suspended solids also seem to be interesting (Table 4). The average zinc concentration in suspended solids in the Vistula section in Nowy Bierun was approximately 0.3 mg Zn/dm^3, which is close to that in waste sludge from municipal waste water treatment plants [12]. Simultaneously, the content of zinc is definitely higher in suspended solids than in other tested sections where there is a clear impact of industrial waste water. High zinc concentrations in suspended solids confirm the PIG data related to zinc contamination of bottom residues. In comparison to other water-courses its content in the Przemsza and Brynica Rivers was extremely high. The highest one was reported in the Brynica River - about 10303 mg Zn/kg dry weight, it was 4364 mg Zn/kg dry weight in the Przemsza River [7]. The values obtained during the discussed tests are higher. These differences are likely to be caused by carbon suspended solids reduction discharged to water in recent years.

Conclusions

This study presents zinc concentrations that have occurred in the water of the Przemsza River and its tributaries in 1994 and 1996. Reported values are highest in Poland and are related to the non-ferrous metal industry located in this river basin. The ICP-AES method was used in the analytical work. The acquired experience confirmed the suitability of this technique in routine analyses of water in a broad range of concentrations.

Zinc concentrations in 1994 were significantly higher and exceeded acceptable standards by several times in all tested sections. This phenomenon should be related to hydrological drought that occurred at that time. Zinc content reported in 1996 was clearly lower.

Zinc occurs both in dissolved form and in suspended solids form in surface water. The dissolved form was approximately 30% of the total content of this element in the

Przemsza River and its tributaries. Simultaneously, the average percentage of zinc in suspended solids fluctuated within the range of 1.3-2.1% and was distinctly higher than the one in the Vistula River upstream the Przemsza River estuary.

References

1. WLODARCZYK J., OSRODKA L. Udzial wod obcych w rzekach wojewodztwa katowickiego. Arch. Ochr. Srod., **1-2,** 39, **1988.**
2. HOLDA I., OSRODKA L. Proba okreslenia odplywu antropogenicznego wybranych rzek wojewodztwa katowickiego. Arch.Ochr.Srod., **1-2,** 73, **1989.**
3. DOJLIDO J. Chemia wody. Arkady, Warszawa, **1987.**
4. KABATA-PENDIAS A., PENDIAS H. Biochemia pierwiastkow sladowych. PWN, Warszawa, **1993.**
5. GALAS W., PISTELOK F. Analytical Problems in Determining Beryllium in Surface Water. Pol. Journ. of Env. Stud., **5,** 29, **1996.**
6. Resolution of the Minister of Environmental Protection, Natural Resources and Forestry dated Nov. 5, 1991 on water classification and standards that have to be met by waste water discharged to water or soil. Dz.U. **116,** poz. **503,** 1579-1583, **1991.**
7. JARZE.BSKI L. Raport o stanie srodowiska w wojewodztwie katowickim w latach 1994. Biblioteka monitoringu Srodowiska, Katowice, **1995.**
8. JARZE.BSKI L. Raport o stanie srodowiska w wojewodztwie katowickim w latach 1995-1996. Biblioteka Monitoringu Srodowiska, Katowice, **1997.**
9. MEINCK F., STOOFF H., KOHLSCHUTTER H. Scieki przemyslowe. Arkady, Warszawa, **1997.**
10. Resolution of the Minister of Health and Social Care dated May 4, 1990 changing the resolution on portable and industrial water standards. Dz.U. **35,** poz. **205,** 479-480, **1990.**
11. BLASZCZYK T, MACISZYKOWA A. Klasyfikacja jakosci zwyklych wod podziemnych dla potrzeb monitoringu srodowiska. Panstwowa Inspekcja Ochrony Srodowiska, Warszawa, **1993.**
12. PISTELOK F., STUCZYNSKI T., DANIELS W.L., PANTUCK K. Aspekty prawne wykorzystania osadow sciekowych. Materialy na konferencje „Postep techniczny w dziedzinie oczyszczania sciekow", Katowice, 12-14. 10. **1995.**