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Występowanie i zmienność mikroelementów w wodzie w podłużnym przekroju rzeki Nidy *

The occurrence and variability of microelements in the water in the longitudinal section of the River Nida

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Abstract — In the water of the River Nida and its clean and polluted tributaries the occurrence of the 10 most important microelements and the general chemical composition were investigated in the characteristic periods of the year. It was found that the inflow of pollution with the waters of the River Bobrza brings about an increase in the content of heavy metals, especially of zinc, chromium, and lead in the water of the Czarna Nida and the Nida. However, the concentration of none of these metals in the water of these two rivers exceeds the limits considered as distinctly noxious for aquatic organisms. The self-purification of these rivers from heavy metals, with the exception of chromium, occurs on a sector of about 40 kilometres. Among other factors it is favourably influenced by the admixture of the clean waters of their tributaries. A certain set-back in the self-purification of the discussed polluted rivers is observed in the winter period. Also a tendency to an increased content of heavy metals in the water is observed with low water levels in the rivers. The content of microelements in the clean tributaries of the Nida, with the exception of strontium, generally corresponds with their content in other clean rivers and chiefly depends on the character of the substratum. In connection with the characteristic geological structure of the catchment basin, the amount of strontium in the water of the whole river network of the Nida is several times higher than in other clean rivers.

In these times of increasing influence of various pollutions on the biological environment the records of the actual level and the processes of circulation of elements occurring in trace amounts in the waters become necessary. In the waters of rivers a knowledge of the amounts

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of such elements may be not only an indicator of the natural geochemical situation or of the pollution occurring in a given landscape, but may also help in the analysis of the ability of self-purification of a river from various contaminations, or in the identification or determination of the place where these contaminations are released into the river.

The determination of the quantitative level of trace heavy metals is above all necessary in the waters which are or will in the future be taken for the purpose of water supply without any more extensive treatment, and which flow in the neighbourhood of larger industrial agglomerations or cities. In several countries in such regions the waters which are destined for water works are already systematically analysed for the content of certain metals (Haberer, Normann 1972). In these countries experimental researches are carried out with the aim of determining the degree of fixing of more toxic metals in the course of water treatment (Reichert et al. 1972). The classic methods for the treatment of drinking water do not secure satisfactory elimination of some noxious heavy metals (Taylor 1971). New methods of their elimination from waste waters are also being developed (Lindstedt et al. 1971).

If the content of heavy metals necessary for the existence of various organisms in the water exceeds the optimal level of concentrations, it begins to act toxically. This negative action is not limited to cases of great excess of this level but may also occur with lesser ones, if only this state lasts for a longer time. This concerns many organisms (An der Lan 1969, Brungs 1969, Jackson, Brown 1970, Cheremisinoff, Habib 1972, Young, Lisk 1972).

In the absence of data on the primary concentration of microelements in the waters and sediments of clean rivers not only observations of the progress in the pollution on the areas of their catchment basins but also a well-timed action against this progress are difficult.

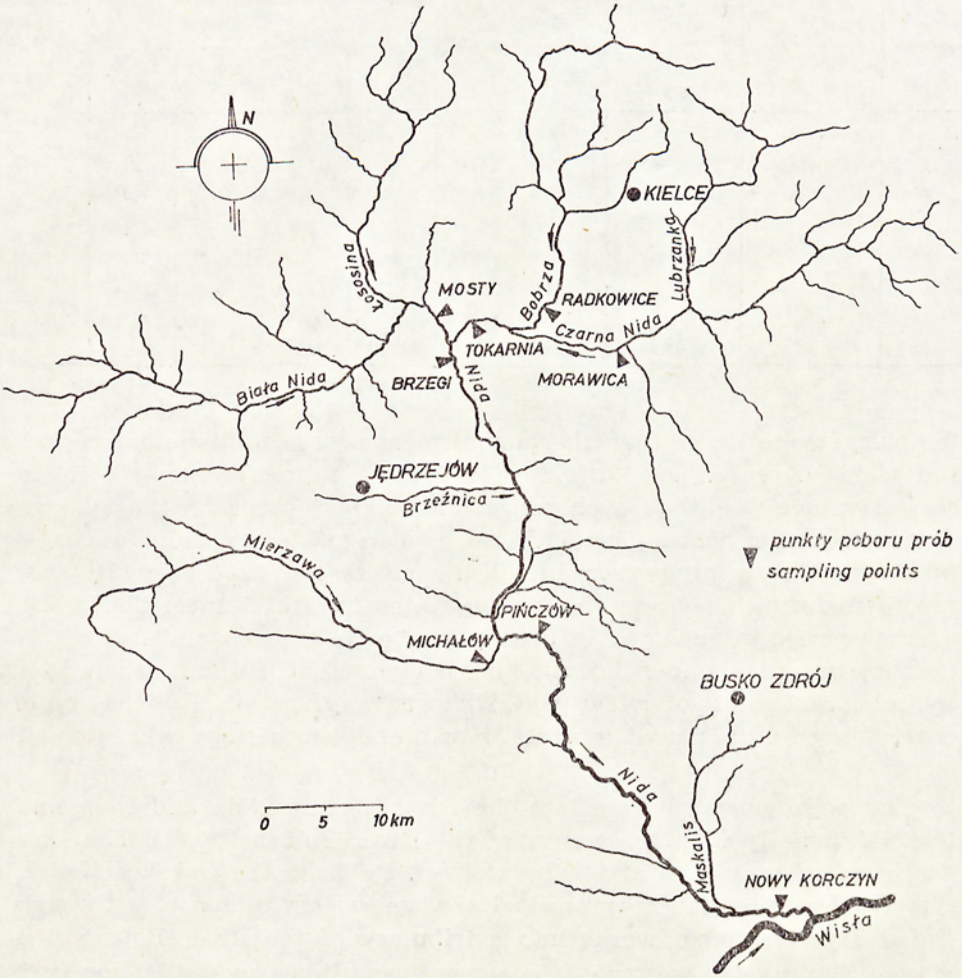
The main object of the presented investigations was to determine the occurrence of more important microelements in larger clean tributaries of the River Nida, on the background of the general chemical composition of their water, as well as the analysis of the degree and rate of self-purification of the water from these elements on the example of the polluted parts of the Czarna Nida and the main River Nida.

Territory and method of investigations

The samples for general chemical analysis and for the content of microelements were taken from the surface layer of the water in the main river and its tributaries in the characteristic periods of various seasons of the year (1971—1972). Only the polluted water of the River

Bobrza was filtered. The river network of the Nida and the arrangement of the sampling stations along the river course are presented in fig. 1.

The content of microelements and of iron was determined using the atomic absorption spectrophotometer (Hemsley 1971, Standard Methods 1971). The condensation of microelements in the water samples was carried out by the method given in detail in an earlier publication (Pasternak 1972). In the majority of cases strontium was determined directly in the crude sample of the water acidified with concentrated HNO_3. The elemental chemical composition of the water was determined



Ryc. 1. Plan sieci wodnej rzeki Nidy i rozmieszczenie punktów poboru prób wody
Fig. 1. Plan of the river network of the Nida and the distribution of sampling stations

using the methods given by Just and Hermanowicz (1964) and Standard Methods (1971).

The values of the yield of the River Nida and its investigated tributaries on the days of water sampling are given in Table I. As the results of all the data of investigations indicate, the yields recorded in the rivers were lower than the annual means for a multiannual period, the yields observed on 19th May 1971 most approximating the mean annual values. Yields of such range (and higher) occur on the average in the Nida for about 3.5 months in a year and are usually observed in the winter-spring period. In all the rivers the lowest yields were recorded during the sampling of the water on 7th October 1971. The average period of such values usually is about 8 months and its greater part occurs in summer and at the beginning of autumn. From the hydrological point of view the Nida is a river of lowland type, characterized with a predominance of winter-spring risings over summer ones.

Tabela I. Przepływy rzek w profilach wodowskazowych w dniach poboru prób wody (wg danych PIHM) na tle średnich rocznych z wielolecia w m^3/sek.

Table I. Yield of rivers in water-gauge profiles on days of collecting water samples (according to data of the Hydro-Meteorological Institute) against the background of the average annual from a multiannual period in m^3/sek.

Rzeka River	Profil Profile	Powierzchnia zlewni Area of catchment basin km^2	Data Date						Średni roczny Average annual
			19.V. 1971	13.VII. 1971	7.IX. 1971	26.X. 1971	29.I. 1972	10.V. 1972	
Czarna Nida	Morawica	758	2.42	1.75	1.50	1.94	1.60	2.17	3.60
Bobrza	Radkowice	378	1.50	1.10	1.10	1.50	1.50	2.20	-
Czarna Nida	Tokarnia	1214	5.68	3.67	3.15	3.94	4.40	5.00	5.93
Biała Nida	Mosty	1033	5.00	3.80	2.30	3.00	2.20	2.40	-
Nida	Brzegi	2260	11.00	7.77	5.30	7.06	6.70	7.77	12.10
Mierzawa	Michałów	562	4.30	3.30	1.25	2.15	1.60	2.05	-
Nida	Pińczów	3354	17.40	11.50	9.88	10.90	9.80	10.40	18.10
Nida	Nowy Korczyn	3863	20.00	13.00	11.50	12.50	11.50	11.00	-

The pollutions penetrate into the River Czarna Nida and then into the Nida chiefly with the waters of the River Bobrza (fig. 1). They are composed of municipal and industrial sewage from the town of Kielce, directly fed through the municipal sewage system and partly through the sewage treatment works into a tributary of the River Bobrza (the stream Silnica); the wastes of the cement- and limestone-mill „Nowiny", and of the tuberculosis hospital at Dobromyśl. Moreover, in its further course the main River Nida receives a small load of the following municipal and industrial wastes: from the town of Jędrzejów (through the stream Brzeźnica, several kilometres long), from the town of Pińczów, from a gypsum plant in Gacki, and from a fruit and vegetable processing plant in Jurków at Wiślica (directly). In the last sector of its course the water of the stream Maskalis brings into it the rest of the unpurified waste mineral sulphate-chloride water, released to this stream by the Phthysiotherapeutic Sanatorium in Busko-Zdrój. At present a small amount of industrial pollution also penetrates to the upper sector of the River Mierzawa from the little town of Sędziszów. In the near future the Nida will also receive a considerable load of sewage from the newly constructed cement works localized in the lower sector of the River Łososina, the main tributary of the River Biała Nida, and the Mierzawa from the new boiler-making plant.

The substratum of the catchment basin of the Czarna Nida, one of the two rivers which give origin to the main River Nida, is for the most part composed of dolomites, limestones, sandstones (also quartzite ones) of various ages (Devonian, Jurassic period) covered with morainic, more rarely with alluvial sands, on some areas of which peat soils were formed in wider valleys.

In the catchment basin of the River Bobrza, besides dolomites and limestones, a mosaic of Triassic red and grey sandstones with loams and Cambrian grey rocks occurs, especially in its upper sector.

The (grey) sandstones in the upper sector and the limestones in the lower one also occur under a layer of sands and muddy-peat soils in the catchment basin of the River Łososina (Wierna Rzeka). However, in the catchment basin of the recipient of the Łososina, the River Biała Nida, marls and chalk limestones covered with various sands and rendzina soils formed on the outcrops of limy rocks, or with valley muddy-peat soils, dominate. Also the marls and limestones partly under sands and partly under loess soils form the majority of the remaining area of the catchment basin of the Nida with its greatest tributary in the middle sector, the River Mierzawa. A uniform area of loess soils which occurs on the whole lower right bank part of the catchment basin of the Nida begins at the right bank of the Mierzawa. On the left bank areas of the Nida catchment basin small areas of Tertiary gypsum and of soils of the kind of sulphurous rendzinas formed on it, occur besides chalk limestones and others covered with sands or rendzina.

Discussion of results

The water of the upper sector of the River Czarna Nida is a clean water of low oxidability, low content of chlorides, weak alkaline reaction, and medium total hardness (Table II). It is also characterized by a low

Tabela II. Chemiczne właściwości wody rzeki Nidy i jej dopływów

Table II. Chemical properties of the water of the River Nida and its tributaries

Rzeka River (Miejscowość) (Locality)	Data Date	Temperatura wody Water temperature °C	pH	Tlen rozpuszczony Oxygen dissolved mg O_2/l	Utlenialność Oxydability mg O_2/l	Alkaliczność Alkalinity meq/l	Twardość ogólna Total hardness °n °G	mg/l						Fe µg/l
								Ca	Mg	K	Na	Cl'	SO_4	
Czarna Nida (Morawica)	19.V. 1971	13.2	8.0	8.64	4.0	2.70	8.8	45.0	10.8	1.12	3.36	7.2	10.1	198
	13.VII. "	19.5	7.8	7.84	3.5	2.75	8.6	45.4	9.8	1.28	3.84	7.0	5.8	135
	7.IX. "	12.9	7.7	9.76	2.9	2.75	8.8	46.4	10.0	1.48	3.36	7.2	7.2	88
	26.X. "	7.9	7.6	9.44	4.1	2.75	9.2	44.3	13.0	1.88	4.00	7.8	15.8	65
	29.I. 1972	0.3	7.2	9.76	1.5	2.85	9.5	47.9	12.1	1.60	4.80	7.0	17.8	162
	10.V. "	13.4	7.6	6.88	4.9	2.30	8.5	42.9	10.8	1.36	3.60	7.7	24.0	375
Bobrza (Radkowice)	19.V. 1971	15.5	7.3	0.16	17.1	3.55	11.0	49.3	17.8	7.76	27.20	41.5	16.8	1112
	13.VII. "	19.3	7.2	0.00	21.8	4.05	12.3	67.2	12.6	6.78	24.40	37.0	10.6	1269
	7.IX. "	13.4	7.3	0.64	27.5	3.90	11.4	62.2	11.7	7.72	28.40	38.5	10.6	3017
	26.X. "	9.1	7.2	0.64	28.2	3.90	11.3	51.4	17.8	8.00	32.80	44.0	13.4	2130
	29.I. 1972	2.4	7.1	2.40	28.8	4.35	12.5	70.0	15.6	11.16	37.60	46.5	33.1	1250
	10.V. "	15.3	7.2	0.16	17.0	3.45	10.1	53.6	11.3	8.60	34.00	43.5	18.2	1500
Czarna Nida (Tokarnia)	13.VII.1971	20.0	7.4	2.56	7.0	3.40	10.7	57.9	11.0	3.32	11.20	17.8	10.6	848
	7.IX. "	14.6	7.3	0.64	16.6	3.60	11.1	54.3	15.1	5.00	17.68	26.0	13.0	1700
	26.X. "	8.6	7.4	6.88	8.6	3.45	10.8	59.7	10.4	4.24	17.60	24.0	14.4	662
	29.I. 1972	0.4	7.2	5.12	7.6	3.60	11.5	54.3	16.9	5.08	19.28	26.2	23.5	375
	10.V. "	15.3	7.3	3.84	9.0	2.85	9.5	50.0	10.8	3.16	13.12	21.2	16.8	707
Biała Nida (Mosty)	19.V. 1971	13.8	7.9	7.04	5.2	3.10	10.1	49.3	13.9	0.84	4.40	10.0	9.6	300
	13.VII. "	19.3	7.8	7.04	5.0	3.10	10.3	67.9	3.3	0.96	5.36	10.2	9.6	145
	7.IX. "	13.2	7.8	9.76	4.0	3.15	10.2	67.2	3.5	1.12	4.96	10.5	7.2	130
	26.X. "	8.3	7.4	9.76	5.6	3.30	10.7	70.4	3.7	1.40	4.40	8.3	8.2	158
	29.I. 1972	0.3	7.3	10.62	2.7	3.30	10.7	65.8	6.5	1.36	6.08	9.5	9.6	395
	10.V. "	13.9	8.0	6.72	4.3	3.10	10.3	62.9	6.5	1.16	4.80	10.2	10.6	450
Nida (Brzegi)	19.V. 1971	14.7	7.6	3.84	5.4	3.30	10.2	45.0	16.9	3.16	10.16	16.5	9.6	320
	13.VII. "	20.6	7.4	3.43	4.7	3.35	10.6	61.8	8.7	2.28	6.48	11.5	8.2	620
	7.IX. "	14.1	7.4	4.16	9.0	3.65	11.2	62.2	10.8	3.72	12.00	19.2	9.1	1407
	26.X. "	8.3	7.7	9.92	5.8	3.35	10.8	68.6	5.2	1.76	5.60	9.8	9.6	150
	29.I. 1972	0.3	7.3	7.20	4.1	3.55	11.1	61.5	10.8	3.20	10.84	16.0	10.6	350
	10.V. "	15.4	7.4	4.16	6.4	3.00	10.0	54.3	10.4	2.80	8.96	15.5	15.4	625
Mierzawa (Michałów)	19.V. 1971	12.1	8.1	8.80	4.1	4.85	15.4	97.2	7.8	1.68	3.20	7.8	6.7	625
	13.VII. "	16.1	8.0	7.68	4.5	4.80	15.3	99.7	5.6	1.84	3.56	7.8	6.7	345
	7.IX. "	11.0	7.8	9.76	3.8	4.95	15.8	103.6	5.6	2.06	3.20	7.8	7.2	100
	26.X. "	7.7	7.8	10.24	4.3	5.00	16.0	100.0	8.7	2.64	4.00	7.5	12.0	100
	29.I. 1972	0.3	7.7	10.40	1.8	4.90	15.8	93.6	11.7	2.20	4.40	7.0	15.4	125
	10.V. "	12.3	8.1	6.88	2.8	4.90	15.8	97.9	9.1	1.84	3.28	7.8	10.6	117
Nida (Pińczów)	26.X. 1971	7.8	7.9	9.76	4.7	3.75	12.5	72.9	10.0	3.04	8.00	13.2	20.2	188
	29.I. 1972	0.3	7.2	4.16	3.0	3.95	12.7	71.5	11.7	3.12	10.56	16.0	15.4	375
	10.V. "	12.2	7.8	6.72	4.2	3.40	11.8	72.2	7.4	2.20	7.52	12.8	24.0	650
Nida (Korczyn)	19.V. 1971	15.9	7.8	7.68	5.4	3.85	13.1	82.2	6.9	2.04	6.88	12.8	20.2	750
	13.VII. "	22.3	8.0	6.56	6.2	3.90	13.0	82.5	6.3	2.24	7.84	13.2	18.2	873
	7.IX. "	12.8	7.3	9.12	3.8	4.00	13.1	82.2	6.9	3.00	9.64	16.2	15.4	100
	26.X. "	8.3	7.8	10.10	5.5	3.90	13.6	82.9	8.7	3.72	12.40	18.8	31.2	325
	29.I. 1972	0.3	7.2	4.00	2.3	4.10	13.5	76.5	12.1	3.26	9.80	15.5	19.2	225
	10.V. "	15.7	7.7	6.24	4.1	3.45	12.7	76.5	8.7	2.60	9.80	14.3	39.4	250

content of potassium and sodium, and — in relation to average waters flowing from territories covered with loose and slightly clayey sands — by a slightly higher content of magnesium. The last named feature results from the occurrence of dolomite rocks in the deeper substratum of the catchment basin of the Czarna Nida, especially in the catchment basin of one of its larger tributaries, the River Belnianka. In the catchment basin of the Czarna Nida in spite of the predominance of sandy soils (in wet valleys) from which iron is relatively most easily leached (among others in the form of complex organic and mineral compounds, Pasternak 1968), and of dolomites containing considerable admixtures of iron minerals, the concentration of iron found in the water is relatively low, the probable reason being that a considerable amount of the compounds of bivalent iron leached from the catchment basin is precipitated in the well-oxidized alkaline waters of this river. This supposition is supported by the occurrence of brown hydroxide films formed on the bottom in the shallower, better warmed zones of this river. Certainly the ferruginous bacteria, which find favourable conditions for development in such zones, are also active here (Hässelbarth, Lüdemann 1971). That part of iron which occurs in the easily soluble stable complex compounds with humus acids remains longer in the water and is analytically determined (Oldham, Gloyna 1969). The filling of a small new shallow reservoir on the River Belnianka, a tributary of the Czarna Przemsza, with sandy soils dominating in its catchment basin, increased still farther the precipitation of iron from the water.

The concentration of microelements in the water of this clean sector of the Czarna Nida is, with the exception of strontium, relatively low and not very variable in time (Table II). In comparison with other clean waters of Polish rivers on sandy substratum (Pasternak, Antoniewicz 1970) the clean water of the Czarna Nida is conspicuous only for a markedly lower content of copper, zinc, and manganese. A small amount of the last named element in the water of the Nida may also partly result from its precipitation together with ferric hydroxides (Solomin, Gončarova 1968, Harris, Troup 1970). The manganese hydroxides $(MnOH)^2$ alone precipitate in a greater measure from the water if the latter reaches a reaction of about 8.5 pH. The low quantitative level of zinc, lead, cadmium, and chromium in the water of this part of the discussed river indicates a still negligible influence of various pollutions in the region of its catchment basin. The influence of „blooming" of plankton algae (blue-green algae) found in this part of the river on the sectors of slowly flowing water, as well as of the partial developmnet of flowering plants submerged in the whole river course, may have no great importance in the above-presented formation of the level of the content of microelements in the water.

It seems that the relatively high content of strontium in the clean water of the Czarna Nida does not so much result from the stronger solubility of $Sr(HNO_3)_2$ than of $Ca(HCO_3)_2$ in the water, as from the slightly increased, in relation to the clark in the lithosphere, amount of this element in the dolomite and calcareous rocks, which dominate in this region, and from its small biological accumulation. Strontium is also weakly adsorbed by various colloids. In the region of the Świętokrzyskie Mountains, from which a great part of the waters of the Czarna

Nida flows (the catchment basin of the River Lubrzanka), a considerable amount of the minerals of strontium (celestite) was also found in the outcrops and veins of the lamprophyre (Daleszyce), in other intrusions of vulcanites, and in metallic minerals occurring in the rocks of these mountains (Szczepanowski 1962). The process of the formation of minerals of strontium during the creation of gypsum and also of calcareous-dolomite rocks is favoured by the limited possibility of building Sr^{+2} ions into the crystal lattice of these rocks (Gaweł 1955, Morawiecki, Domaszewska 1956, Ważny 1969).

From the place of inflow of the strongly polluted River Bobrza (fig. 1) the River Czarna Nida carries considerably polluted waters (Table II). The relation of the volume of the polluted waters of the Bobrza to the clean ones of the Czarna Nida amounts to about 1 : 1.5. Above all, with the water of the Bobrza a large load of organic sewage passes into the Czarna Nida. In consequence the BOD_5 of the Czarna Nida increases from the most often recorded value of 1.0—3.5 to the range of 5.0—17.0 mg O_2/l and the oxidability from 1.5—4.0 to 7.0—16.0 mg O_2/l. At the same time on this sector of the Czarna Nida a great decrease in the amount of the dissolved oxygen and in the reaction occurs (Table II). In certain periods in the community of the water microflora a mass development of *Sphaerotilus natans* is observed.

For the general characterization of the degree of contamination of the River Bobrza it is worth noting that in the sector near the outflow the BOD_5 of its water ranges from 8—16 in the spring-summer period and from 20—35 mg O_2/l in the autmun-winter one, while, as may be seen from Table II, the oxidability of its water is of the order 17—28 mg O_2/l during the whole year. The water of the River Bobrza also carries a considerable amount of various suspended solids and of dissolved mineral compounds. Among mineral macrocomponents great amounts of iron, sodium, chlorine, potassium, calcium, and magnesium occur, and among microcomponents zinc, chromium and lead. The pollution from the centre of the cement and lime industry mentioned above — that fed with waste waters directly to the river as well as that deposited in the form of dusts and washed by the rain from the surface of soils and plants — greatly contributes to the increase in the amount of potassium, calcium, and magnesium in the water of the Bobrza. The emission of dusts from this centre amounts to about 600 t/24 hrs. The dusts contain 40—48 per cent $CaCO_3$ and 5 per cent K_2O, as well as significant amounts of some trace elements. As may be seen from the works of Dobrzański et al. (1970) the deposition of dusts of the cement-mill Wierzbica brought about an increase in the content of some microelements, especially of strontium and manganese, in the surface layers of the neighbouring soils.

Besides the increase in the indices of organic pollution and the deterioration of oxygen conditions in the waters of the Czarna Nida below the outflow of the Bobrza, a manifold increase in the content of iron, sodium, and potassium in relation to the upper sector of the river occurred. The total hardness and the content of microelements in the water also increased. Above all in the composition of microelements in the polluted water of the lower sector of the Czarna Nida, a strong increase in the content of zinc, chromium, manganese, and lead (Table II) is observed. As the result of a considerable dilution of the waters of the Bobrza the concentration of neither of the investigated heavy metals in the water of the Czarna Nida reaches the level which is at present considered as distinctly noxious for aquatic organisms. This is further demonstrated by the fact that in this sector the water of the Czarna Nida shows, as was already mentioned, considerable hardness and buffering, these properties neutralizing the toxicity of the heavy metals. The toxicity of the heavy metals or their biological accessibility are in a great measure favourably influenced by the presence in the water of this part of the Czarna Nida of great amounts of various organic substances which can form complex compounds with them. Nevertheless, in the periods of low water levels (July, September) in the water of the lower section of the Czarna Nida the concentration of chromium and zinc is already of such a range that it may be considered as the factor decreasing the class of purity and the practical value of this water. Up to the present the data on the negative influence of chromium (Cr-VI and Cr-III) on the aquatic environment of rivers are very scare in the literature. It may be inferred from the review of results presented by Haberer and Normann (1971) that the majority of authors postulate 50 μg Cr-VI/l as the limit for drinking waters. Slight differences in the chromium content between the polluted waters of the Bobrza and the Czarna Nida suggest some additional source of pollution of the Czarna Nida localized just above the sampling stations in Tokarnia (perhaps a tannery). The concentration of copper as well as of zinc and lead in the water of the Bobrza and in the lower sector of the Czarna Nida is less than might have been anticipated on the basis of the industrial pollution, probably because under bad oxygen conditions of the environment of these rivers (especially in the canals bringing in the wastes), these elements precipitate into the bottom sediments in the form of poorly soluble sulphides. It is possible that a part of these elements is absorbed by fine suspended solids and eliminated from the water by the sedimentation along the course of the rivers.

The content of manganese, molibdenium, cobalt, and iron in the water of this part of the Czarna Nida, though much higher than in the clean upper sector, is still within the range of levels with which the small aquatic organisms participating in the process of the purification of the water are stimulated by these elements. Besides the presence of a sufficient amount of phosphorus in the environment an increased content of microelements is also required for the intense development of the bacteria and algae which accompany the processes of purification of the water from organic substances. On the example of Lake Ontario, Chau et al. (1970) found that along with the high concentration of trace amounts, especially of manganese, the content of chlorophyll increases, this being considered as one of the indices of the development of algae in the water. The experiments of Gavalas and Clark (1971) indicate that an insufficient content of manganese may not only result in the inhibition of photosynthesis and development of a plant organism, but also in its greater susceptibility to organic inhibitors which usually abound in municipal sewage. Among such organic inhibitors are the detergents (Davis, Gloyna 1969). Molibdenium is particularly necessary for the optimal development of bacteria and alage. As Vega et al. (1971) indicate, this element is essential for the normal action of the complex of nitrate reductase in the alga cells.

About 4 kilometres below the sampling station in Tokarnia the polluted Czarna Nida unites with the clean River Biała Nida (supplied by a large tributary, the River Łososina), forming from this place the River Nida proper (fig. 1). The average relation of the waters of the Czarna Nida to the Biała Nida amounts to 1:0.7 (Table I).

The water of the Biała Nida is characterized by (Table II): weak alkaline reaction, good oxygenation, small content of potassium, magnesium, and sodium, of chlorides and sulphates, medium content of iron, and a content of calcium considerably higher than in the clean water of the upper sector of the Czarna Nida (on account of the different geological structure of the catchment basin). It also has higher oxidability and colour than the clean water of the Czarna Nida. The increased colour and oxidability of the water of this river is connected with the occurrence of greater amounts of humus compounds, especially in the spring period, leached from the peat soils which cover considerable areas in its main valley as well as in the valley of its tributary the Łososina. It is worthy of note here that the colour of the humus compounds occurring in the water not only depends on their amount but also on the pH value of the water: it becomes more intense with the increase of pH (Gjessing 1971).

The content of microelements, with the exception of strontium, in the water of the Biała Nida corresponds with the most usual quantitative range of these elements in the clean waters of rivers and lakes (Chawla et al. 1969, Pasternak, Antoniewicz 1970, Haberer, Normann 1971). However the average amount of almost all investigated microelements is slightly higher in the water of the Biała Nida than in that of the clean sector of the Czarna Nida. As far as the amount of copper, zinc, and manganese is concerned, the water of the

Biała Nida is also slightly richer than that of the inflowing River Łososina (Pasternak, Antoniewicz 1971). Strontium occurs in the water of the Biała Nida in increased amounts, considerably exceeding its average content in the rivers of the Soviet Union (Stradomskij, Konovalov 1968). This undoubtedly results from the dominance of calcareous rocks in the substratum of the catchment basin of this river; as was mentioned above, they contain great amounts of primary minerals or of isomorphous admixtures of this element (celestite $SrSO_4$).

At the beginning of the River Nida itself a further decrease in the content of organic matter, expressed by the fall of the value of BOD_5 to 3.5—7.0 and of the oxidability to 7—16.6 mg O_2/l, occurs in the water. It must be mentioned here that the decrease in the value of these indices is much greater than might be attributed to the process of self-purification of the river on this sector of several kilometres. In a great measure it is brought about by the dilution of the polluted water of the Czarna Nida by the clean water of the Biała Nida, the value of the oxidability decreasing in a relatively smaller degree than that of the BOD_5. This probably resulted from the natural oxidability of the water of the Biała Nida, higher than that of other rivers in this region.

In this part of the Nida the concentration of the individual mineral macrocomponents in the water also changes (Table II). As opposed to the changes in the amount of organic substances this fact is not so much the result of the more intense action of a biological factor under better physico-chemical conditions (stronger oxidation, transparency of the water) as of the admixture of the water of the Biała Nida, possessing its characteristic chemical properties.

Above all, in the composition of the macroelements of the water a decrease in the amount of magnesium, potassium, sodium, chlorides, and sulphates, and an increase in calcium and carbonates occurs in this sector of the Nida. However, in the water of the Nida the decrease in the amount of magnesium and increase in calcium occurs in such a proportion that the total hardness of the water is almost the same as in its chief tributaries — the Czarna and Biała Nida. Besides, as an effect of the better oxidation and higher pH of the water in this part of the Nida than in the lower sector of the Czarna Nida, intense precipitation of iron originating from pollution, and its considerable decrease are observed.

In the water of the initial sector of the Nida considerable changes in the content of microelements are also recorded (Table III). On the whole, it may be observed that their concentration distinctly decreases — with the exception of strontium and barium. Especially the content of zinc, copper, manganese, and cobalt in the water decreases. This probably

Tabela III. Zawartość pierwiastków śladowych w wodzie rzeki Nidy i jej dopływów w µg/l

Table III. Content of trace elements in the water of the River Nida and its tributaries in µg/l

Rzeka River (Miejscowość) (Locality)	Data Date	Cu	Zn	Pb	Cd	Mn	Cr	Co	Mo	Sr	Ba
Czarna Nida (Morawica)	19.V. 1971	1.8	15	5	1.2	50	–	–	–	–	–
	13.VII. "	11.0	77	15	2.5	28	3.1	1.0	6.7	575	82
	7.IX. "	2.5	18	6	1.2	20	4.3	1.7	6.2	525	109
	26.X. "	2.0	13	9	0.8	17	1.3	1.8	5.6	625	100
	29.I. 1972	2.5	18	5	2.5	18	1.1	1.9	2.5	400	50
	10.V. "	2.0	19	6	1.3	107	1.3	2.0	2.5	750	63
Bobrza (Radkowice)	19.V. 1971	10.0	170	34	2.5	94	–	–	–	–	–
	13.VII. "	17.6	1200	20	3.7	300	81.3	3.3	7.5	600	125
	7.IX. "	15.0	462	40	1.8	191	100.0	3.9	8.8	695	104
	26.X. "	11.0	329	36	2.0	160	100.0	2.5	4.4	675	88
	29.I. 1972	8.7	127	19	3.0	119	15.0	2.8	8.8	800	112
	10.V. "	9.8	268	20	2.5	225	25.0	9.5	7.5	625	75
Czarna Nida (Tokarnia)	13.VII.1971	13.0	170	22	2.5	180	50.0	2.5	7.0	750	95
	7.IX. "	12.0	178	19	2.5	150	81.2	3.0	6.3	713	100
	26.X. "	6.0	93	19	1.7	144	50.0	2.0	5.0	700	83
	29.I. 1972	5.0	73	13	2.2	128	13.0	2.3	7.5	600	150
	10.V. "	5.8	57	10	1.8	105	25.0	9.0	6.8	825	75
Biała Nida (Mosty)	19.V. 1971	5.2	15	10	2.5	60	–	–	–	–	–
	13.VII. "	7.5	25	7	2.0	14	3.8	1.8	6.7	1825	112
	7.IX. "	3.7	13	9	1.0	11	6.3	2.1	5.8	1785	125
	26.X. "	2.0	31	16	1.3	12	3.8	2.0	6.3	950	100
	29.I. 1972	8.5	48	22	2.7	189	1.3	2.2	6.2	1520	112
	10.V. "	2.0	27	10	1.2	50	1.2	2.5	2.5	1200	100
Nida (Brzegi)	19.V. 1971	5.2	25	20	2.0	64	–	–	–	–	–
	13.VII. "	15.0	75	12	2.0	195	43.7	2.0	6.3	875	100
	7.IX. "	6.3	146	16	1.7	135	75.0	2.5	6.0	757	104
	26.X. "	2.0	25	16	1.3	19	43.7	2.2	7.2	1050	93
	29.I. 1972	3.7	38	13	2.0	150	12.5	2.2	5.0	1020	125
	10.V. "	5.0	63	11	1.3	100	13.0	6.0	5.5	950	88
Mierzawa (Michałów)	19.V. 1971	5.2	20	15	2.5	33	–	–	–	–	–
	13.VII. "	8.7	100	21	3.0	33	5.0	2.7	6.8	3000	125
	7.IX. "	2.5	82	23	2.5	16	12.5	3.7	11.2	3035	156
	26.X. "	2.0	37	14	1.5	22	4.8	2.7	6.2	3000	105
	29.I. 1972	2.5	56	25	3.0	50	2.5	2.5	6.3	2720	138
	10.V. "	2.0	15	10	1.3	30	2.5	6.5	5.0	1800	150
Nida (Pińczów)	26.X. 1971	2.0	33	12	0.8	25	43.7	2.5	4.4	2100	93
	29.I. 1972	3.7	46	13	2.5	440	18.8	2.2	7.8	1520	100
	10.V. "	9.0	28	14	1.0	105	25.0	3.0	15.0	1800	125
Nida (Nowy Korczyn)	19.V. 1971	5.2	21	10	1.8	78	–	–	–	–	–
	13.VII. "	4.3	220	15	2.0	88	43.7	1.7	6.7	2500	125
	7.IX. "	2.5	19	9	1.3	21	81.2	3.8	9.0	3570	146
	26.X. "	2.0	20	16	1.3	40	37.5	2.5	5.0	2500	113
	29.I. 1972	3.7	26	13	2.5	200	18.7	2.1	6.2	1600	125
	10.V. "	2.0	15	8	1.3	50	12.5	3.5	3.8	1700	112

results not only from the fact that their content is low in the water of the Biała Nida, which flows in higher, but also from their biological accumulation, relatively stronger here than in the polluted sector of the Czarna Nida. Under more favourable physico-chemical conditions of this zone of the Nida, besides bacteria and fungi, various groups of green algae may in a greater measure join in the processes of self-purification, these elements, as has already been mentioned, being necessary for the intense development of such organisms. It should be noted here that, according to Dokulil (1971), among such algae the blue-green algae generally reveal a slightly higher resistance to an oxygen deficit. As the works of Martin (1970), carried out in the clean ocean waters, indicate, apart from phytoplankton the zooplankton plays an important role in the elimination of heavy metals from the water. Besides intensively catching bivalent elements such as Zn, Cu, and others (among others by surface sorption and building into skeleton structures, which after dying off settle on the bottom) this group of aquatic organisms also accumulates considerable amounts of lead, in spite of the fact that this element does not play any determined physiological function. In comparison with phytoplankton the sea zooplankton accumulates much less manganese (Rožanskaja 1968).

Similarly as in the case of iron, in the upper sector of the River Nida manganese can also partly precipitate from the water physico-chemically, as the result of great changes of the oxidation-reduction potential and of the pH in the water, brought about by the inflow of the well-oxidized water of the Biała Nida. On the intensively precipitating ferric and manganese hydroxides a certain amount of other heavy metals may also be adsorbed and transferred to the sediment (Harris, Troup 1970). As the experiments of Solomin and Gončarova (1968) with nickel indicate, such adsorption increases with the increase in the pH of the solution. In a considerably smaller measure chromium decreases in the water of the initial sector of the Nida. Strontium and barium appear in the water of this part of the Nida in even greater amounts than in the Czarna Nida. The admixture of the waters of the Biała Nida, very rich in these elements, chiefly contributes to this.

About 38 kilometres later the River Nida is supplied by its next large tributary, the River Mierzawa. However, the share of the Mierzawa in the total volume of the water of the Nida is slight. On the average it amounts to 1 : 4.8 of the volume.

The water of the Mierzawa shows an alkaline reaction, low oxidability, small amounts of sodium, potassium, chlorides, and sulphates, usualy an average content of iron and manganese (the left bank part of the catchment basin composed of sands), and a high, the highest of all the investigated water courses, content of calcium (Table II).

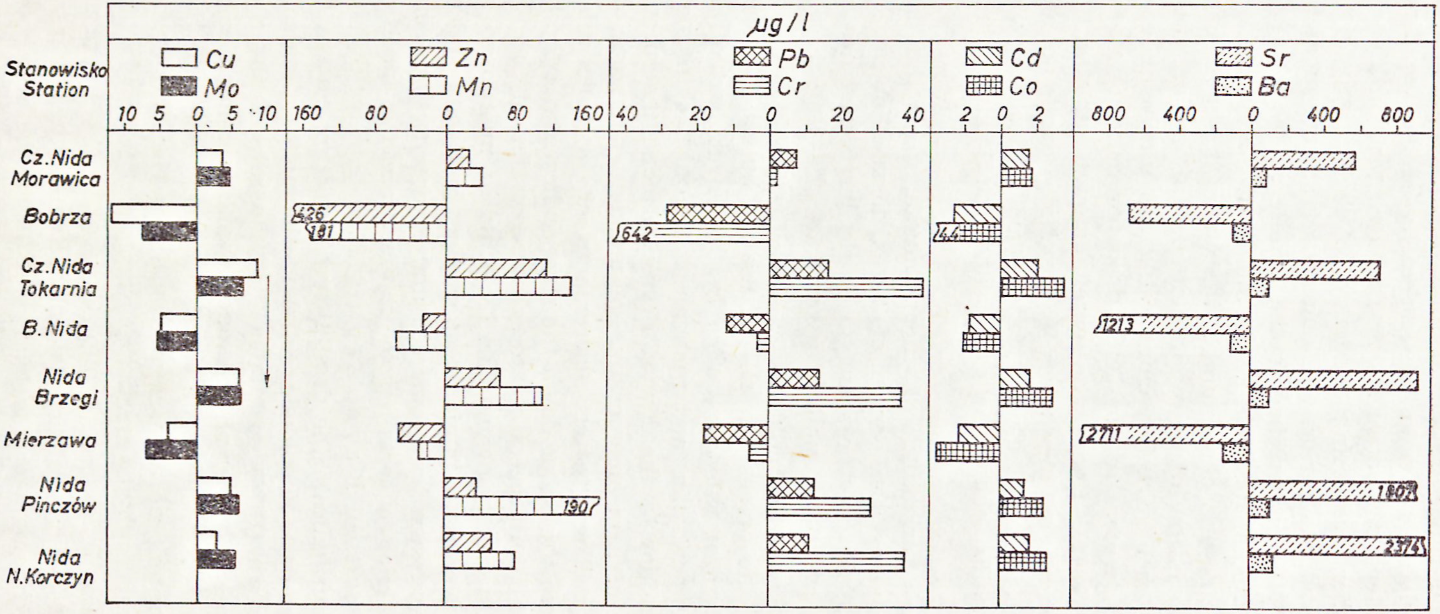
The quantitative level of individual microcomponents in the water of this river is not uniform (Table III). Similarly as in other clean tributaries of the Nida, the content of copper, manganese, and molibdenium is low but of other trace elements distincly higher. This mostly concerns strontium, zinc, lead, and chromium. The highest increase in the content of these few microelements is found in this river in the periods of low water levels. A distinct increase in the quantitative level of some heavy metals in the water of the Mierzawa indicates the influence of mineral pollution in this river. It may be that the source of this pollution are the industrial establishments and metal workshops localized in the town of Sędziszów. The exceptionally high concentration of strontium in the water of the Mierzawa is connected with the occurrence of soft rocks rich in calcium (marls, loesses) in the substratum of the catchment basin. The elemental chemical composition of the water of the Nida several kilometres below the outflow of the Mierzawa, i. e. near the town of Pińczów, changes in a very small measure, chiefly in connection with the not very great masses of the water of this tributary. In the water of the Nida an increase in the amount of calcium and a decrease in the oxidability (Table II) and the BOD_5 (to the value of 3.0—4.5 mg O_2/l) only are noted.

In this sector of the River Nida the concentration of individual microelements changes in a higher degree, these changes being above all expressed by a further increase in the content of strontium and barium (compare the water of the Mierzawa), by an increase in the content of manganese in some periods, and by a considerable quantitative decrease in all other investigated heavy metals. The periodical increase in the concentration of manganese in the water of the Nida may result from the sporadically greater than usual inflow of waters from the swamps and wet sandy meadows spreading for many kilometres in its valley. In this sector of the Nida the influence of the polluted stream Brzeźnica does not appear in the content of heavy metals in the water. Probably after several kilometres of its course the stream undergoes significant self-purification.

In the water of the sector of the Nida near the outflow an increase in the indices of organic pollution is again observed, i.e. of the BOD_5 (3.6—5.5 mg O_2/l) and oxidability (Table II), as well as of the content of sodium, chlorides, and iron. It seems to be connected with the renewed inflow of various pollutions from towns and industrial establishments localized in the lower half of the catchment basin (mentioned in the introduction). Moreover, in the water of this sector of the river a further increase in the amounts of calcium and a decrease in magnesium occurs. The main reason of such proportions between these macroelements is the inflow of waters from the left bank gypsum territories, which are not great in respect of volume but conspicuous in their very great content of calcium. The content of calcium in the stream Maskalis which flows in the gypsum territories amounts to about 172 mg Ca/l (according to Wróbel 1964), and in the Karst waters to about 390 mg Ca/l, according to the data of the present author. It is characteristic that in the water of this part of the Nida the content of sulphates does not increase in such a degree as might be inferred from the type of water of the neighbouring tributaries. This interesting phenomenon will be discussed, however, in another work by the author.

In the lower course of the Nida (between Pińczów and Nowy Korczyn) the inflow of a new load of pollution and the separate qualitative character of the geological-soil structure of the substratum of this part of the catchment basin bring about a partial change in the trend of the formation of the concentrations of microcomponents in the water. Namely, the concentration of some microcomponents, such as zinc, chromium, cobalt, and cadmium (especially of the two first), once again increases instead of decreasing, as it did so far. With the flow of the river, a further decreasing tendency is shown only by copper, manganese, and lead. As far as the amount of strontium and barium is concerned, it is still higher than in the middle course of the river at Pińczów. In the sector of the Nida at the mouth of the river the increase in the content of zinc and chromium in the water is almost exclusively connected with the inflow of new pollutions in this region, the content of zinc in the water of Karst streams being not much higher than in other pure surface waters of the Nida drainage basin (Pasternak, Antoniewicz 1970). Hence the great amount of strontium and barium in the water of this part of the Nida must be above all connected with the inflow of ground-waters (readily leaching weathered gypsum, exceptionally rich in celestite, and the loamy rocks which accompany it).

The degree of variability of mean amounts of the individual microcomponents along the course of the Czarna Nida and Nida is presented in fig. 2. As may be seen, the fairly large load heavy metals which penetrates with the polluted water of the Bobrza undergoes successive decrements along the course of these rivers, this being the result not only of the process of self-purification but also of its dilution by the clean waters of the tributaries. In the lower part of the river the content of copper, zinc, and manganese diminishes in the highest and that of chromium in the lowest degree. Among macrocomponents the concentration of iron, magnesium, sodium, and potassium decreases most significantly. The greatest decrements of biogenic micro- and macroelements from the water down the river indicate that the biological factor dominates in the process of the self-purification of the Nida from higher concentrations of heavy metals. It should be mentioned here that in this lowland river with numerous old river beds and shallow bank zones, usually overgrown by submersed and emergent flowering plants, the higher plants play a certain role in the process of purification of the water. The results of Karaseva (1971) and of Rodziller and Zotov (1971) even indicate the possibility of utilizing certain flowering plants (*Scirpus lacustris, Typha latifolia*) in the purification of sewage. However, Nümann (1970) postulates that the role of these plants is much less than that of periphyton and of the communities of other small organisms in it. Among others, Varenko and Čujko (1971) determine the content of more important microelements in the most common aquatic macrophytes and Stečenko and Pomilujko (1971) in the algae of the blue-green group. Cowgill (1970) presents very interesting results of investigations on certain higher plants in the circulation and economy of some heavy metals in the water of a lake.



Ryc. 2. Średnie zawartości mikroelementów w wodzie wzdłuż biegu Czarnej Nidy i Nidy (prawa strona diagramów) oraz w ich dopływach (lewa strona diagramów). Strzałka oznacza kierunek przepływu wody

Fig. 2. Average contents of microelements in the water along the course of the Czarna Nida and Nida (right hand side of the diagrams) and their tributaries (left hand side of the diagrams). The arrow indicates the direction of the water flow

This author draws attention, for instance, to the great role of *Lemna minor* here and to the correlation between the development of this plant and the concetration of zinc in the lake water.

It seems that the relatively slight decrease in the amount of chromium recorded in the lower parts of the Nida results chiefly from the dilution of the load of pollution by the clean water of the tributaries, the coefficient of the biological absorption of chromium being low while greater amounts of chromium influence unfavourably the organisms which take part in this process (Bailey et al. 1970). It must be mentioned here that the dilution with clean water of the load of pollution released into the river cannot be accepted as the proper method of neutralization of the pollution of the aquatic environment.

The variability of the concentration of strontium and barium along the course of the river is quite the reverse. The content of both these elements (not basically connected with the inflow of pollution but with the quantitative differentiation of the substratum of the catchment basin) systematically increases with the flow of the river.

Conclusions

1) The inflow of municipal and industrial pollution with the water of the River Bobrza brings about a considerable increase in the concentration of heavy metals in the water of the Czarna Nida and the main River Nida, especially of zinc, chromium, and lead.

2) However, in the polluted water of the Czarna Nida and the Nida the level of the concentration of none of these metals exceeds the values accepted as distinctly noxious for living organisms. The class of the purity and of the usability of the water of the polluted lower sector of the Czarna Nida and of the initial one of the Nida may only be reduced by the phenomenon of the increasing concentration of zinc and chromium at low water levels.

3) No distinct correlation is found between the concentration of the majority of the investigated heavy metals in the water and the value of the indices of the general pollution, especially of the organic one, in the water. Only a tendency towards dependence of the concentration of such metals on the water level may be observed (in July and September with low water levels the concentration of certain metals in the water was higher).

4) As the distance from the point of inflow of the main pollutions grows, the content of microelements in the water of the Czarna Nida and Nida decreases, with the exception of strontium and barium. A new

rise in the amount of certain metals in the water of the lower sector of the Nida indicates the inflow of a new load of pollution in this region.

5) The decrease in the content of the majority of the investigated microelements, with the exception of chromium, in the water of the Nida to such a quantitative level as in the clean tributaries occurs on a sector of about 40 kilometres, the present ability of the River Nida for self-purification being fairly high. Among other factors it is favourably influenced by the admixture of a great mass of clean water from the tributaries. A slower rate of purification of the river from various pollutions and hence an elongation of the sector of purification may be observed in the winter period.

6) The amount of iron and manganese originating from the pollution decreases most intensively in the water of the Nida on the sector of the first significant amelioration of its oxidability and of the increase in the pH — i.e. in the region of the station at Brzegi.

7) The content of the determined microelements, with the exception of strontium, in the pure tributaries of the Nida generally corresponds with their concentration in other clean rivers and mainly depends on the quality of the catchment basin.

8) In connection with the characteristic geological structure of their catchment basin, the level of concentration of strontium in the water of the Nida and its tributaries is several times higher than in other clean rivers.

STRESZCZENIE

Zbadano w wodzie rzeki Nidy i jej czystych i zanieczyszczonych dopływach występowanie 10 ważniejszych mikroelementów oraz ogólny skład chemiczny w charakterystycznych porach roku (tabela II i III). Celem tych badań było między innymi prześledzenie na przykładzie zanieczyszczonej części Czarnej Nidy i głównej rzeki Nidy stopnia i tempa samooczyszczania się wody z metali ciężkich. Zawartość mikroskładników wody oznaczano za pomocą atomowego spektrofotometru absorpcyjnego. Dla pełniejszego obrazu sytuacji geochemicznej panującej w zlewniach poszczególnych cieków, podano ich krótką geologiczno-glebową charakterystykę. Wartości przepływów wody w rzekach w dniach poboru prób zestawiono w tabeli I.

Między innymi stwierdzono, że dopływ komunalnych i przemysłowych zanieczyszczeń z wodą rzeki Bobrzy wpływa na znaczne podwyższenie stężenia metali ciężkich w wodzie Czarnej Nidy i głównej rzeki Nidy, zwłaszcza cynku, chromu i ołowiu. W zanieczyszczonej wodzie tych dwu rzek ilość żadnego z badanych śladowych metali nie przekracza jednak wartości uznawanych za wyraźnie szkodliwe dla organizmów żywych. Niemniej jednak stężenie chromu i cynku w wodzie dolnego odcinka Czarnej Nidy osiąga w okresach niskich stanów wody (lipiec, wrzesień) już taki poziom, że można go uznać za czynnik obniżający klasę czystości i wartość użytkową tej wody. Zawartość większości badanych metali ciężkich w wodzie nie wykazuje wyraźnej korelacji z wartością wskaźników ogólnego zanieczy-

szczenia wody, zwłaszcza organicznego. Daje się jedynie zauważyć tendencja zależności stężenia takich metali od stanu wody w rzece. W miarę oddalania się od punktu dopływu głównych zanieczyszczeń, zawartość mikroelementów w wodzie Cz. Nidy i Nidy, z wyjątkiem strontu i baru, sukcesywnie maleje (ryc. 2). Ponowny wzrost w wodzie dolnego odcinka Nidy niektórych metali wskazuje na dopływ w tym rejonie nowego ładunku zanieczyszczeń. Obniżenie zawartości większości badanych mikroelementów w wodzie Nidy do takiego ilościowego ich poziomu jak w czystych dopływach następuje, z wyjątkiem chromu, na odcinku około 40 km. Aktualna zdolność rzeki Nidy do samooczyszczania jest więc dość znaczna. Między innymi wpływa na to dodatnio domieszka dużej masy wody jej czystych dopływów (rozcieńczenie stężeń składników). Przy tym podkreślono, że rozcieńczanie zrzuconego do rzeki ładunku zanieczyszczeń czystą wodą nie może być przyjmowane jako właściwa metoda przeciwdziałania zanieczyszczeniu środowiska wodnego. Pewne zwolnienie szybkości oczyszczania się rzeki z różnych zanieczyszczeń i skutkiem tego wydłużenie odcinka jej oczyszczania daje się zauważyć w okresie zimowym. Ilość żelaza i manganu pochodzenia zanieczyszczeniowego najbardziej maleje w wodzie Nidy na odcinku pierwszego znacznego polepszenia się jej natlenienia oraz podwyższenia pH (rejon Brzegów).

Zawartość badanych mikroelementów w czystych dopływach Nidy, z wyjątkiem strontu, na ogół odpowiada ich koncentracji w innych czystych rzekach i kształtuje się głównie w zależności od jakości podłoża. Najmniej mikroskładników ma woda czystego odcinka rzeki Cz. Nidy. Poziom stężenia strontu w wodzie Nidy i jej dopływów w związku z charakterystyczną budową geologiczną ich zlewni (dużym zasobem w skałach celestynu) jest kilkakrotnie wyższy niż w innych czystych rzekach. Zawartość strontu i baru z biegiem rzeki systematycznie wzrasta.

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