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Zawartość miedzi, cynku i manganu w wodzie zbiornika zaporowego w Goczałkowicach oraz kilku innych zbiorników

The content of copper, zinc, and manganese in the water of the dam reservoir at Goczałkowice and of several other reservoirs

Wpłynęło 27 maja 1970 r.

Abstract — The content of Cu, Zn, and Mn was determined in the water of various zones of the reservoir at Goczałkowice, of the river Vistula supplying it, and in the water of the outlet. For comparison, the concentration of these microelements was also determined in waters of seven other dam reservoirs (pure and polluted). It was found that the content of all the investigated elements in the Goczałkowice reservoir is higher than in the pure Carpathian reservoirs, showing a distinct horizontal, vertical, and seasonal differentiation. The seasonal variability of these elements depends to some extent on the meteorological conditions of the surrounding terrain. None of these differentiations show any distinct relationship with the other, simultaneously determined chemical properties of the water. The inflow of microcomponents into the reservoir is greater than their outflow. Mineral pollution has the greatest effect on the content of microelements.

The increased pollution of the aqueous medium noted of late encourages the intensification of observations also on the content of mineral microcomponents in surface waters (indicator of the degree of pollution of the river basin). The recording of the concentration and circulation of trace elements is particularly necessary in the waters of dam reservoirs designed for water-supply purposes. These elements can have a detrimental effect on the quality of such waters not only when the permissible concentrations are exceeded (toxic action), but also when they occur in still admissible quantities, being, however, already capable of stimulating excessively the development of bacteria and algae (Ruttner 1963, Hutchinson 1967). In some productive water reservoirs with a limited exchange of water (lakes, ponds, reservoirs) there may also occur deficiencies of assimilable microelements. This phenomenon is often related with the high content in the water of organic matter capable of forming with these elements complex compounds.

Detailed data necessary to determine more accurately the course and range of all the phenomena mentioned above are still scarce in the available literature. This is probably due not only to the considerable differentiation of the alimentary demand for microcomponents by the particular species of hydrobionts, or else their varying resistance to the toxic action, but also to the simultaneous antagonistic or synergetic action with the other elements and substances present in water. Many interesting data concerning these problems are found in Wiessner's (1962) synthetic work, as well as in those of Goldman (1960), Ingols and Fetner (1961), Garder and Skulberg (1966), Suchovierchov (1967), Veličko (1968, 1968a), Nachšina et al. (1968), Ishac and Dollar (1968), Parker and Hasler (1969), Kožar (1969), Stangenberg and Szulkowska-Wojaszek (1970).

According to Veličko (1968) and Nachšina et al. (1968), of the more important heavy metals occurring in water zinc is the most toxic. The approximate threshold of toxicity of this metal determined by Veličko (1968) for blue-green algae of the genus *Microcystis* amounts to 0.1—0.2 mg/l. It has recently been accepted that the toxicity of zinc begins already from the concentration of 0.1 mg/l, and this for many groups of aquatic organisms. According to the Polish standards now in force the content of zinc and copper in drinking water (I class of purity) ought not to exceed 0.01 mg/l. Manganese at higher concentrations acts more toxically on algae (*Microcystis*) when it occurs in water in anion form (Veličko 1968a). Symptoms of a deficiency of copper, zinc, and manganese in cultures of algae of the genus *Chlorella* occur, as was reported by Wiessner (1962) after Walker, when the concentration of these elements falls below 10^{-7} M. In media containing the chelating agent the requirements of some algae with regard to zinc amounted to 10^{-1}—10^{-2} mg/l (within the range of 10^{-6} M, Wiessner 1962). Broadly speaking, in the opinion of Brandford et al. (1968), the influence of microelements is often most distinctly marked in waters with a low content of mineral salts.

The problem of the occurrence of microelements in inland surface waters has not as yet aroused much interest in this country. Almost no investigations have been carried out so far (with the exception of manganese) on the content of microcomponents in dam reservoirs.

The aim of the present work was above all to determine the content and distribution of some more important microcomponents in the water of the dam reservoir at Goczałkowice. To obtain a comparable material the concentration of these microelements in pure and polluted waters of seven other dam reservoirs was also investigated. Simultaneously, some other chemical properties were determined in the waters of all these reservoirs.

The Goczałkowice reservoir (upper Vistula) serves for water-supply and retention purposes. The maximum area of the reservoir amounts to 3200 ha and its capacity to 168 mln m^3. The mean depth is about 5.2 m. It is a reservoir of plain type (foreland of the Carpathians) with a small multiplicity of water exchange, amounting to 1.9. Besides the Vistula, a small, partly artificial stream (Bajerka) flows into it from the right bank. This stream receives water from the Vistula, with which it is connected above the reservoir in the locality Harbutowice. During the autumn season a large mass of water is brought in both to the Vistula and Bajerka from complexes of carp ponds which are numerous in this region. The fluctuations of the water level of the Goczałkowice reservoir in 1969 are represented on a diagram (fig. 3) in the further part of this study.

Methods of investigation

Samples of water for these investigations were collected in 1969 from May to October at roughly monthly intervals. This was usually carried out on days when the water of the river and of the reservoir was relatively pure (containing no large amount of mineral suspension). Waters containing suspension were sedimented (in a darkened place) and separated from the deposit. The samples of water from the river and from the outflow of the reservoir were collected with the aid of clean plastic containers and in the reservoir with a 5-litre bathometer also made of plastic. The points of sampling water for analyses were marked on the plan of the reservoir (fig. 1). All samples of water in horizontal section were taken at a depth of about 1.0 m. This layer of water in shallow lakes and reservoirs usually shows a greater primary production than the surface layer (Czeczuga 1964, Bucka 1965). In the vertical section of the water of the reservoir (fig. 1, point 1), in its deepest zone near the dam, the samples were collected from the surface layer, from a depth of 1.0, 2.5, and 5.0 m. The latter level was usually just above the bottom. To determine the influence of pond water on the content of microcomponents in the water of the Vistula, samples from this river were collected during the autumn season above and below the outflow of pond waters. The samples of water (mean) from all the other investigated dam reservoirs were taken only from the depth of 1 m in the zone near the dam.

The microcomponents were concentrated by evaporating 1 l of water, acidified with a few drops of HNO_3 (analysed for the content of the investigated components). The dry residue was diluted in 25 ml of 0.2 n HNO_3. The content of microcomponents in the dilution was determined according to the method of atomic absorption spectroscopy. This method has the virtue (among others) of being very accurate and not sensitive to the action of the background (Walsh 1955, Piccolo and O'Connor 1968). For comparative purposes the content of microcomponents in water both filtered and not filtered through a microbiological washed with acid filter was determined (Coli 5). The other chemical determinations of water were carried out according to the method reported by Just and Hermanowicz (1964) and to the Standard Methods (1955).

Description of the character of the substratum of the catchment basin and of the meteorological conditions of the reservoir at Goczałkowice

The principal source of microelements in surface waters are the rocks and soils of their substratum, as well as industrial wastes and dusts. Thus the average level of concentration of these elements in waters chiefly depends on the quality of the substratum and the degree of pollution of the medium (Pasternak, Antoniewicz 1970). Meteorological conditions also can have a considerable influence on the quantity of microcomponents in waters. This is due to the fact that a number of phenomena (chemical erosion of the catchment basin, water stage, intensity of biological sorption) are connected with them, having a bearing on the content of all electrolites in the water.

About 40 per cent of the area of the catchment basin (532 km^2) is occupied by wooded mountainous areas (Carpathians — Silesian Beskid), 30 per cent by cultivated terrains of the Upland, and the remaining by level country. The mountainous terrain is built of little permeable sandstone-schist rocks with a predominance of siliceous and clay cement, on which various loam soils developed. The substratum of the Upland is formed of Cieszyn shales and limestones, loess loam, and Carpathian gravel, covered with silt soil little resistant to erosion, containing carbonates on only small areas. The level part of the basin is entirely covered with silt deposits poor in alkaline compounds, mostly of aquatic origin (Pasternak 1962).

The mountainous area of the catchment basin is characterized by an exceptionally large precipitation (1000—1300 mm). Owing to this and to the very small stream system on the terrain of the Upland, the amount and quality of water of the Vistula and of the reservoir is chiefly determined by the mountainous area of the catchment basin. Data concerning the meteorological conditions of the terrain adjacent to the reservoir are presented in Table I. As can be seen from it, the period of investigations was characterized by a slightly lower air temperature in relation to the multiannual period and by a greater precipitation in June and August (in the second half), and an unusually low one in September and October.

Tabela I. Charakterystyka warunków meteorologicznych na terenach przyległych do zbiornika w 1969 r.

Table I. Characteristics of meteorological conditions on terrain adjoning the reservoir in 1969

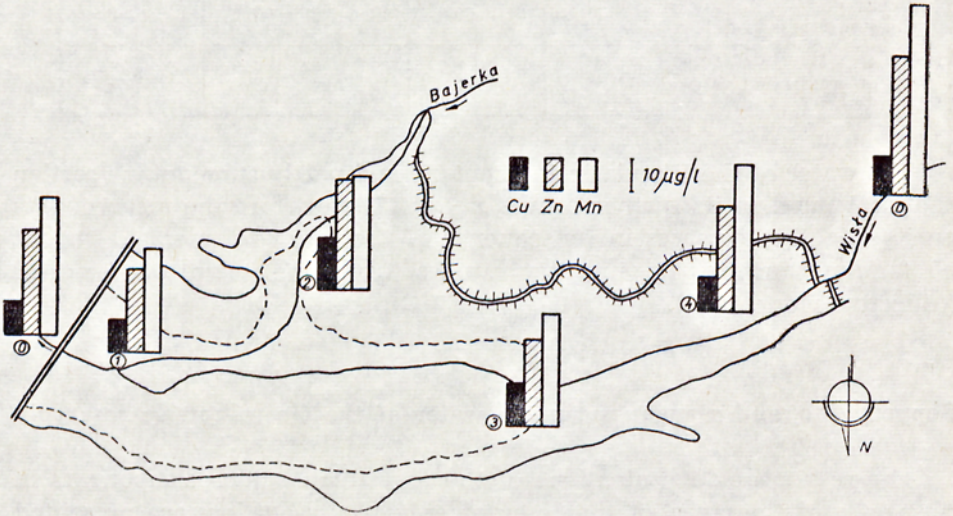
Parametry meteorologiczne Meteorological parameters	Miesiące Months						
	IV	V	VI	VII	VIII	IX	X
Średnia miesięczna temperatura powietrza °C Mean monthly air temperature °C	7,5	15,3	15,4	18,1	16,1	14,1	8,8
Odchylenia temperatury powietrza od średniej wieloletniej °C Deviations of air temperature from the multiannual mean °C	-0,6	1,9	-0,9	-0,3	-1,4	0,3	-0,2
Usłonecznienie (sumy miesięczne godz./doba) Insolation (monthly total h./24 h.)	175	228	144	223	186	195	128
% wartości wieloletniej usłonecznienia % of multiannual value of insolation	120	124	77	106	92	120	106
Opad (mm) Precipitation (mm)	19,6	98	152	97	159	7	26
% wartości wieloletniej opadu % of multiannual value of precipitation	86	101	120	82	135	9	42

The water of the Vistula in its montane and partly submontane section is almost pure. In its further course, about 17 km before the reservoir, its purity slightly decreases in consequence of the inflow of a small amount of tanning and textile industry wastes from the town of Skoczów (collective work, 1965).

Copper, zinc, and manganese in the water of the Goczałkowice reservoir

The results of determinations of the investigated microcomponents in the water of the river, of the reservoir, and of its outflow are presented against the background of other chemical properties of these waters in Table II. As can be seen from these data, the content of copper in the water supplying the reservoir ranged from 7.63 to 15.45, that of zinc from 22.75 to 70.20, and that of manganese from 18.75 to 133.50 µg/l. The content of copper in the water of the reservoir varied between 5.95 and 25.5, that of zinc ranging from 16.50 to 46.00, and that of manganese from 12.10 to 64.80 µg/l. Thus, the least differentiated in the water of the river was the content of copper and that of manganese the most. In the water of the reservoir the content of copper varied the most and that of zinc the least. For comparison, it is worth noting that in the water of the Rybinsk dam reservoir on the upper Volga the content of copper ranged from 1.0 to 6.2

and that of manganese from 5.0 to 80.0 µg/l (Kolcov 1965), while in the water of the Volgograd reservoir (lower Volga) it varied from 3.5 to 15.5 µg Cu/l and 0—5.5 µg Mn/l (Krasnov and Kuzmenko 1967). A larger amount of copper in the water of the Rybinsk reservoir (15.0 µg Cu/l) was noted by Kolcov only in the region of the inflow of wastes from the town of Cherepovets. The mean seasonal contents of copper and manganese in the water of the Goczałkowice reservoir is also much higher than the corresponding mean content of these components in the pure waters of the Cimliansk and Veselovski reservoirs, and of the polluted Staro-Beshevski reservoir (Dacko et al. 1964; Dacko and Krasnov 1964, 1965). The content of zinc in the relatively pure waters of the Uglicheski and Rybinsk reservoirs varied from 6 to 35 µg Zn/l, whereas in the polluted water of the main zone of the Ivanovski reservoir it ranged from 9 to 120 µg Zn/l and in the region of the inflow of concentrated industrial wastes from the town of Kalinin amounted up to 540 µg Zn/l (Kalinina 1969).



Ryc. 1. Średnia zawartość miedzi, cynku i manganu w wodzie różnych stref zbiornika oraz w wodzie dopływu (D) i odpływu (O).

Fig. 1. Mean content of copper, zinc, and manganese in the water of various zones of the reservoir and in the water of the inflow (D) and outflow (O)

The mean concentrations of the examined microelements in the water of the river, in that of various zones of the reservoir, and in the water flowing out from it, are presented in fig. 1. As can be seen from it, the horizontal distribution of these elements in all the mentioned aqueous media shows considerable differences. Taken as a whole, the largest number of microelements occur in the water of the river, somewhat less

Tabela II. Zawartość miedzi, cynku i manganu w wodzie zbiornika goczałkowickiego na tle innych właściwości chemicznych wody w 1969 r.
a - powyżej dopływu głównej masy wód stawowych b - poniżej dopływu

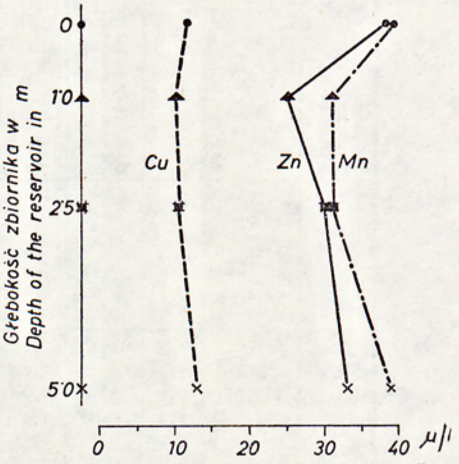
Table II. Content of copper, zinc, and manganese in the water of the Goczałkowice reservoir against the background of other chemical properties of the water in 1969
a - above the affluent of main mass of pond waters b - below the affluent

Punkt pobrania wody Water sampling point	Data Date	pH	Tlen rozpuszczony Oxygen dissolved mg $O_2/1$	Alkaliczność Alkalinity me/1	Twardość ogólna °n Total hardness °G	Utlenialność Oxydability mg $O_2/1$	Fe mg/1	Cu	Zn	Mn
								µg/1		
D Dopływ (rzeka Wisła) Affluents (river Vistula)	6.V	7,4	8,58	0,80	3,70	3,28	0,36	13,13	25,75	18,75
	3.VI	7,4	–	1,25	5,40	2,52	0,40	8,52	70,20	60,70
	11.VII	7,3	9,92	0,90	4,30	3,12	0,34	15,45	42,50	19,44
	28.VIII	7,2	–	0,80	4,15	3,20	0,08	7.63	22,75	133,50
	29.IX	7,1	–	1,60	6,30	4,32	0,70	11,38	43,75	37,24
a	28.X	6,7	–	1,15	5,10	6,32	0,84	11,62	43,20	71,60
b		7,4	–	2,00	7,40	13,04	0,48	13,95	63,20	114,00
Potok Stream Bajerka	28.VIII	6,9	8,20	0,80	3,10	4,60	0,40	9,60	50,20	82,50
4 Górna część zbiornika Upper part of the reservoir	6.V	8,1	10,24	0,98	4,14	4,80	0,22	5,95	19,50	40,00
	3.VI	7,3	–	1,10	4,45	4,80	–	10,25	39,00	57,20
	11.VII	7,3	10,08	0,95	4,50	4,00	0,19	17,25	43,00	28,32
	28.VIII	7,2	–	0,90	4,20	4,80	0,03	7,50	27,50	29,05
	29.IX	–	–	–	–	–	–	–	–	–
	28.X	7,3	–	1,05	4,70	5,04	0,24	10,46	27,50	64,80
3 Środkowa część zbiornika Middle part of the reservoir	6.V	8,3	10,69	1,04	4,20	4,00	0,21	11,90	24,25	37,25
	3.VI	7,6	8,48	1,08	4,65	4,16	–	14,25	35,37	43,00
	11.VII	7,6	9,28	1,05	4,50	5,00	0,24	17,25	25,20	14,72
	28.VIII	7,3	–	1,00	4,40	4,32	0,04	9,38	26,80	43,70
	29.IX	7,3	–	1,05	4,50	4,24	0,22	9,10	16,50	13,26
	28.X	7,3	–	1,05	4,80	5,76	0,16	15,12	28,70	52,90
2 Zatoka Bajerki Bajerka bay	6.V	8,4	10,69	1,02	4,30	4,32	0,20	15,48	23,50	40,00
	3.VI	7,6	8,64	1,12	4,65	4,32	–	25,50	16,80	39,20
	11.VII	7,3	8,64	0,95	4,40	4,80	0,28	20,80	34,50	14,16
	28.VIII	7,3	8,96	1,00	4,30	5,40	0,08	8,75	41,00	53,30
	29.IX	7,3	8,96	1,00	4,40	4,48	0.22	6,26	46,00	12,32
	28.X	7,2	10,72	1,05	4,70	7,32	0,17	11,62	32,70	42,40
1 Przyzaporowa część zbiornika Part of the reservoir near the dam	6.V	8,2	11,10	1,12	4,37	4,24	0,15	7,15	28,30	37,25
	3.VI	7,6	8,80	1,12	4,67	4,48	–	13,65	30,50	39,20
	11.VII	7,4	8,16	1,00	4,40	3,88	0,10	13,10	24,80	28,32
	28.VIII	7,3	8,96	1,00	4,40	6,00	0,04	6,50	19,25	15,46
	29.IX	7,3	8,96	0,95	4,40	4,64	0,18	11,48	18,75	12,10
	28.X	6,7	10,08	1,05	4,70	8,56	0,12	8,13	27,50	52,00
0 Odpływ Effluent	6.V	7,3	10,88	1,10	4,45	4,00	0,15	9,52	38,0	30,00
	3.VI	7,6	8,48	1,08	4,65	4,64	–	13,65	32,50	87,50
	11.VII	7,4	8,96	0,95	4,40	4,00	0,10	16,65	46,90	14,72
	28.VIII	7,3	–	1,00	4,45	4,88	0,06	8,13	29,50	63,10
	29.IX	7,4	–	1,05	4,55	4,48	0,24	6,97	19,50	30,10
	28.X	7,3	–	1,05	4,80	5,48	0,16	5,69	18,75	18,12

in the uper part of the reservoir, and the least in its deepest zone near the dam. In most cases the water of the river is above all richer in manganese and zinc. Judging from the horizontal distribution of microcomponents in the water of the reservoir it appears that the water of the Vistula acts only on its upper part. A similar horizontal distribution of microcomponents also occurred in the water system of the Rybins reservoir (Kolcov 1965). An exception to this trend of distribution in the Goczałkowice reservoir is copper. Its content in the water of the middle part, especially in the shallow (3 m) inlet of Bajerka, is higher (much higher in the two periods June and July) than in the water of the river. The results obtained do not explain this phenomenon. It seems, however, that the influence of the quality of water of the Bajerka stream has to be excluded. This stream carries an inconsiderable mass of pure water of the Vistula and apart from country wastes receives no great amount of pollution, even seasonally. On the other hand, it is highly probable that this phenomenon is related in some measure with the increased undulation and presence in this widest zone of the reservoir in June and in the first half of July of a greater quantity of colloidal suspension which, by reducing light, inhibits the development of plankton absorbing copper. The aeolian mixing of water and the resultant raising of sediments from the bottom, followed by their passing to the water masses, also increases at the same time the dissolution of copper present in the sediments. The decrease in the amount of microcomponents in the upper part of the reservoir, rather sudden in relation to the river, can be attributed only in small measure to the flowering vegetation developing in this zone. This kind of aquatic vegetation draws microcomponents chiefly from the bottom (Boyd 1969).

The content of copper in the water of the outflow of the reservoir (lower outlets) is similar to its average amount in the zone near the dam, whereas the manganese and zinc content is slightly higher. However, the amount of the last mentioned components in the water of the outflow does not reach the level of their content in the water of the river. Taken as a whole, the balance of the investigated microcomponents proves to be positive, their inflow being larger than the outflow. It is only copper which accumulates in a very insignificant degree. This was also observed by the author in sediments examined in the same year.

In spite of the considerable aeolian mixing of the water of the Goczałkowice reservoir, there also occurs in it a distinct vertical differentiation of the amount of microelements (Table III). On the average, the layer of water at the depth of 1 m contained the least amount of the investigated microcomponents, and the surface layer, as well as that near the bottom, the largest amount (fig. 2). At the depth of 1 m the content of zinc decreases the most, that of manganese slightly less, and that of copper the least. In some cases a similar decrease in the amount of microcomponents, especially of copper and manganese, occurred in the water of the reservoir at a depth of 2.5 m (Table III). The comparison of the mean content of microelements in the surface layer and in the layer near the bottom showed that manganese occurs in them in similar quantities, while slightly more copper is present near the bottom and zinc near the surface. The lower content of zinc in the layer of water near the bottom of the reservoir, whose medium has mostly a very weak-alkaline reaction (Table II), is probably related with its adsorption by the bottom sediments fairly rich in clayey matter. This seems to be evidenced by the higher content of this component in the sediments of the Goczałkowice reservoir than in those of other pure Carpathian reservoirs (unpublished data of the author). The considerable capability of bottom sediments of adsorbing zinc ions was noted by Feldman and Nachšina (1967) and Duke et al. (1968).



Ryc. 2. Zróżnicowanie średnich ilości miedzi, cynku i manganu w pionowym przekroju wody zbiornika goczałkowickiego.

Fig. 2. Differentiation of the mean amount of copper, zinc, and manganese in the vertical section of water of the Goczałkowice reservoir

The content of microelements in the water of the Goczałkowice reservoir also varies in the course of the season. The most variable is the content of manganese and the least that of zinc. Similarly distinct seasonal changes were noted in the content of cobalt in the waters of lakes of the USA (Parker and Hasler 1969). The seasonal variability of all the investigated microelements shows no distinct correlation either with that of their content in the water of the river (Table II) or with the seasonal fluctuations of the water level in the reservoir (fig. 3). On the other hand, it shows a certain relationship with some more important meteorological parameters. As can be seen from the comparison of the mean quantities of microcomponents in the water of the reservoir in the particular seasons with the monthly total of precipitation and insolation on the areas adjoining it, more microcomponents usually occurred in the water during the cooler and rainy spring-time (May, June) and in late autumn, and less in the summer months and in the very warm and sunny September (fig. 3). A

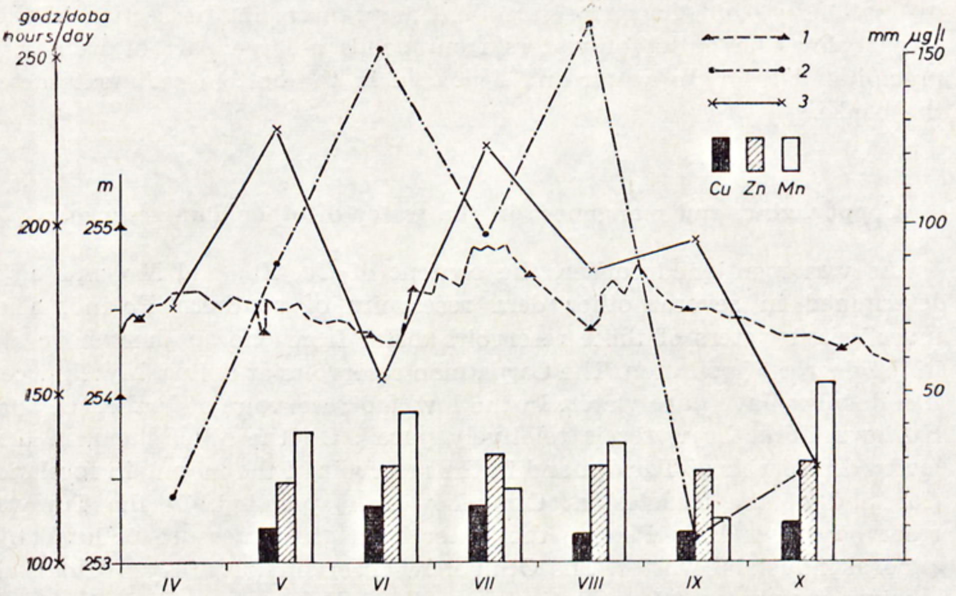
Tabela III. Pionowe rozmieszczenie miedzi, cynku i manganu w wodzie zbiornika w Goczałkowicach (w przyzaporowej części, punkt nr 1 - ryc. 1)

Table III. Vertical distribution of copper, zinc, and manganese in the water of the reservoir at Goczałkowice (part near the dam, point No 1, fig. 1)

Głębokość w m Depth in m	Data Date	pH	Tlen rozpuszczony Oxygen dissolved mg O_2/l	Alkaliczność Alkalinity me/l	Twardość ogólna Total hardness °n °G	Utlenialność Oxydability mg O_2/l	Fe mg/l	Cu	Zn	Mn
								µg/l		
0 m	6.V	8,2	10,78	1,10	4,70	4,32	0,13	8,95	34,20	53,75
	3.VI	-	-	-	-	-	-	-	-	-
	11.VII	7,4	8,16	1,00	4,40	3,80	0,10	13,62	29,80	42,40
	28.VIII	7,3	8,96	1,00	4,50	6,48	0,04	8,88	30,00	34,00
	29.IX	7,3	8,96	0,95	4,40	4,32	0,08	10,80	18,75	18,22
	28.X	7,3	10,08	1,10	4,80	6,80	0,14	13,95	81,50	47,40
1,0 m	6.V	8,2	11,10	1,12	4,37	4,24	0,15	7,15	28,30	37,25
	3.VI	7,6	8,80	1,12	4,67	4,48	-	13,65	30,50	39,20
	11.VII	7,4	8,16	1,00	4,40	3,88	0,10	13,10	24,80	28,32
	28.VIII	7,3	8,96	1,00	4,40	6,00	0,04	6,50	19,25	15,46
	29.IX	7,3	8,96	0,95	4,40	4,64	0,18	11,48	18,75	12,10
	28.X	6,7	10,08	1,05	4,70	8,56	0,12	8,13	27,50	52,00
2,5 m	6.V	8,2	10,69	1,12	4,40	3,92	0,07	8,35	21,00	65,00
	3.VI	7,6	8,64	1,12	4,60	4,48	-	10,25	46,20	35,70
	11.VII	7,4	8,16	1,00	4,40	4,72	0,11	16,10	36,70	14,16
	28.VIII	7,3	8,80	1,00	4,40	5,95	0,08	6,63	33,25	12,13
	29.IX	7,3	8,96	1,00	4,40	4,24	0,10	13,65	18,50	10,20
	28.X	7,3	10,08	1,05	4,80	6,24	0,12	8,13	25,00	46,60
5,0 m	6.V	7,5	9,50	1,14	4,40	4,00	0,19	9,53	23,75	40,00
	3.VI	7,6	8,48	1,12	4,60	4,24	-	15,95	29,30	43,00
	11.VII	7,3	7,52	0,95	4,40	4,72	0,12	22,10	47,20	56,60
	28.VIII	7,3	8,00	1,00	4,50	5,08	0,08	8,88	57,50	29,15
	29.IX	7,3	8,96	1,00	4,50	4,16	0,10	12,50	16,50	27,20
	28.X	7,2	10,08	1,05	4,08	5,12	0,15	8,72	25,00	37,30

higher content of manganese in the spring than in the summer-time as well as in September, was also noted by Krasnov and Kuzmenko (1967) in the water of the Volgograd reservoir. Since meteorological conditions act the strongest (apart from the water level) on the biological processes in the reservoir, the data reported above permit the assumption that the quantitative seasonal variations of copper, zinc, and manganese in its water are caused in great measure by the seasonal changes in the course of these processes. On the other hand, as was established by Parker and Hasler (1969), the role of biological sorption in the formation of cobalt in the waters of lakes is rather insignificant. These authors assign a larger share to physicochemical factors in the binding of this element.

As can be seen from the data presented in Table II, the quantitative differentiation shows no distinct relationship with the other investigated



Ryc. 3. Średnia zawartość Cu, Zn, Mn w wodzie zbiornika goczałkowickiego w poszczególnych terminach (μ/l) na tle wahań poziomu jego wody oraz miesięcznych sum opadów (mm) i usłonecznienia (godz./doba) na terenie przyległym. 1. poziom wody; 2. opad; 3. usłonecznienie

Fig. 3. Mean content of Cu, Zn, and Mn in the water of the Goczałkowice reservoir in the particular periods (μ/l) against the background of the variations of the level of its water and of the monthly total of precipitation (mm) and insolation (h/24 h) on the adjoining terrain. 1. water level; 2. precipitation; 3. insolation

chemical properties of water. A certain tendency to such a relationship can be observed only between microcomponents and the amount of dissolved oxygen. It may be that this relates in some degree to the very small (with the exception of the water of the river during the period of draining ponds) variability of the chemical properties of the investigated waters and to the inflow of a certain amount of pollution. The lack of relationship between the content of microcomponents and oxidability treated as approximate indicator of the development of plankton organisms absorbing these components, probably results from the fact that the oxidability of water is determined not only by the content of the living organic mass, but also to a high degree by the variations of the amount of organic matter (humic, wastes) dissolved in the water. The relationship of microcomponents with the magnitude of production of phytoplankton in water could perhaps be detected if it were possible to make use for this purpose of the values of this production measured by the amount of chlorophyll. In the water of the river during the period of inflow of pond waters (28th September — 28th October) the most marked was the increase in oxidability, total hardness, iron, and manganese. In the section of the river below the outlet of waters from ponds a large part of iron was precipitated from the water and deposited in the bottom sediments near the banks.

Copper, zinc, and manganese in the water of other dam reservoirs

As was mentioned earlier, the content of Cu, Zn, and Mn was also determined in several other dam reservoirs of southern Poland. The investigated waters of these reservoirs differ from one another above all in the degree of pollution. The Carpathian reservoirs at Solina, Myczkowce, and Rożnów have pure water. In the lowland reservoirs at Przeczyce and Kozłowa Góra the water is relatively pure [1]. On the other hand, in the lowland reservoir at Turawa and in the reservoir of the mountain foreland (foreland of the Sudetes) at Otmuchów it is polluted. In the Turawa reservoir (river Mała Panew) the water is in great measure polluted by mineral industrial wastes. The Otmuchów reservoir (river Nysa Kłodzka) receives mostly organic pollution from the cellulose-paper industry, and in the autumn, from the sugar industry. A characteristic trait of the two polluted waters is a fairly intense colouring, resulting from the presence in them of a considerable amount of dissolved humic compounds.

The results of analyses of the content of microelements and of other chemical properties of the water of the mentioned reservoirs are presented in Table IV. As can be seen from these data, the amount of copper in the pure Carpathian waters ranged from 5.58 to 9.75, that of zinc from 13.5 to 27.0, and of manganese from 15.5 to 102.0 µg/l. This shows that the content of microcomponents in these waters, especially that of zinc and copper, was relatively low. The removal from the water of the Rożnów reservoir by filtration of the essential living and dead organic mass had no significant effect on the result of the analysis of the content of microcomponents.

In the waters of the lowland reservoirs at Przeczyce and Kozłowa Góra the content of the examined microcomponents is generally a little higher than in the absolutely pure waters of the Carpathian reservoirs. There occurs in them above all a larger amount of manganese. The higher content of this component in the waters of these reservoirs (in spite of their considerable alkaline reserve) is presumably related not so much with the inflow of a small amount of pollution as with the predominance of sandy deposits in the substratum of their catchment basins. As was already earlier reported (Pasternak, Antoniewicz 1970), waters flowing

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[1] In August copper was applied in these reservoirs in order to overcome the excessive development of algae.

Tabela IV. Zawartość miedzi, cynku i manganu w wodzie innych zbiorników zaporowych południowej Polski

Table IV. Content of copper, zinc, and manganese in the water of other dam reservoirs of Southern Poland

Nazwa zbiornika Name of reservoir		Głębokość w m Depth in m	Data Date	pH	Alkaliczność Alkalinity me/1	Twardość ogólna Total hardness °n °g	Utlenialność Oxydability mg O_2/1	Fe mg/1	Cu	Zn	Mn
									µg/1		
Solina	górna część upper part	1,0	16.IX	8,0	2,1	6,4	3.3	0,03	6,26	23,00	44,10
	dolna część lower part			7,9	2,0	6,1	3,2	0,02	5,69	23,25	43,20
Myczkowce		1,0	17.IX	7,8	2,0	6,2	3,1	0,04	6,82	27,00	38,66
Rożnów		1,0	4.IX	8.0	2,3	7,5	3,4	0,02	9,75	22,50	102,00
			7.X	8,0	2,4	8,3	3,3	0,03	5,58	13,5	15,5
woda sączona percolating water				–	–	–	–	–	5,35	15,0	16,4
Przeczyce		1,0	27.X	8,1	2,5	11,5	21,3	0,06	12,78	36,3	155,0
Kozłowa Góra		1,0		7,4	2,0	9,5	22,2	0,30	9,30	40,0	72,8
Turawa		1,0	5.XI	7,2	1,55	7,2	14,4	1,60	32,55	108,0	278,4
Otmuchów		1,0	6.XI	7,4	2,55	9,6	43,2	1,00	15,70	55,0	136,8

from such strongly permeable sandy terrain usually contain a fairly large amount of manganese.

The highest content of microcomponents was noted in polluted waters of the reservoirs at Turawa and Otmuchów, being much higher in the water of the first mentioned, which receives mineral pollution. The water of the reservoir at Turawa contains a particularly large amount of zinc and manganese. Here the content of zinc exceeds the permissible limit for waters of second class purity, i.e. designed for supplying the needs of farm animals, of watering resorts, and of some branches of industry. Although the catchment basin of the Turawa reservoir is mostly covered with sands, it seems that the exceptionally high content of manganese in its water is above all the result of the inflow of pollution. The water of the reservoir at Otmuchów, polluted with organic matter (high oxidability), differs the least from the pure waters of the Carpathian reservoirs in the content of copper. A similarly low amount of this component was also noted in other surface waters strongly polluted by organic sewage (Pasternak, Antoniewicz 1970). The essential cause of the relatively low content of copper in organically polluted waters are probably the biochemical processes of its precipitation into residue in the form of poorly soluble sulphites, taking place in the bad oxygen conditions usually prevailing in sewage conductors. The low content of copper in the polluted water of the Otmuchów reservoir may also be partly the result of the intensive biological sorption. A considerable development of various plant organisms participating in the process of purification of water is noted in the reservoir during the whole year. On the other hand, it seems that the complex copper-organic compounds usually occurring in this kind of water, containing large amounts of dissolved organic compounds, have no essential effect here. In sea water such copper compounds can, as was reported by Williams (1969), represent 0—28 per cent of the total amount of this element. In the polluted waters of the Turawa and Otmuchów reservoirs a fairly high content of iron was also noted (Table IV).

Recapitulation

As can be seen from the data reported, the content of the particular investigated microelements in the water of the Vistula and of the Goczałkowice reservoir varied within various ranges. The least variable in the water of the river was the copper content, while that of manganese underwent the greatest fluctuations. In the water of the reservoir the content of copper was the most changeable and that of zinc the least. The considerable amplitude of fluctuations of manganese in the water of the Vistula can be explained by the more favourable conditions (greater variability of temperature and of the O_2 content) in the river than in the reservoir for its physicochemical precipitation from the water and by the inflow of pollution and pond waters. The fairly equalized content of zinc in the water of the reservoir is presumably related with the compensating action (sorption) of clayey matter occurring in the bottom.

The average content of copper, zinc, and manganese in the water of the Goczałkowice reservoir greatly exceeds the amount of these components in the pure waters of the investigated Carpathian reservoirs (Tables II and IV). This is probably due to the regular pollution of the Vistula. On account of the lack of data on the content of microelements in the water of this river from the period preceding the filling of the reservoir (1955), the degree of quantitative changes in time of these elements under the effect of pollution cannot be determined. On the basis of the data obtained it can only be assumed that the increased level of concentration of these microelements in the water of the reservoir is an important potential factor stimulating the excessive development of algae, which is greatly detrimental to the water supply system. A mass appearance of algae in this reservoir becomes still more likely to occur on account of the regular accumulation in it of microcomponents and of their more rapid leaching from the bottom in consequence of the fairly strong aeolian mixing of water. For, as it was found, the inflow of microcomponents with the water of the river is greater than their outflow. The mean seasonal content of copper, manganese, and zinc in the water of the Goczałkowice reservoir is also much higher than the respective mean amount of these components in the pure waters of all the above mentioned Soviet reservoirs.

The concentration of microelements in the water of the Goczałkowice reservoir showed a distinct horizontal, vertical, and seasonal differentiation. Investigations of the horizontal variability of the content of these elements in the water of the reservoir together with that of the river showed that on the average they occurred in the greatest amount in the water of the river, in a slightly smaller one in the upper part of the reservoir, and in the smallest in its lower part (fig. 1). An exception here was copper, much more of it occurring in two periods in the middle part of the reservoir than in the upper one (which increases the mean value of copper for this zone). This presumably is chiefly due to the inhibition in these periods of phytosynthesis in the middle zone of the reservoir, on account of the presence in it at that time of a considerable amount of suspension raised from the bottom during the strong undulation. In the vertical section of the water of the reservoir the least amount of all microcomponents was usually noted at a depth of about 1 m and the greatest in the surface layer and in the layer near the bottom. Taking into account the mean values, it was found that in the vertical section of water the most variable was the zinc content (fig. 2). The seasonal differentiation of the content of microelements in the water of the Goczałkowice reservoir showed a certain relationship with some more important meteorological phenomena, which had a considerable influence on the development of aquatic organisms (fig. 3, Table I). Taken as a whole, relatively more microcomponents occurred in the water of this reservoir during the little insolated, rainy, or cool periods (X) than in the sunny and warm ones.

None of the noted differentiations of the content of microcomponents in the water of the Goczałkowice reservoir showed, with a few exceptions, any distinct relationship with the other investigated chemical properties of water (oxidability, total hardness, iron). These differentiations are rather related, as some data indicate (vertical variability and dependence of the seasonal differentiation on meteorological agents) with the intensified development of aquatic algae and inflow of pollution.

Pollution has a particularly strong effect on the increase in the content of zinc and manganese in the waters of the investigated reservoirs (Table IV). The occurrence of manganese in these waters also depends in great measure on the character of the substratum of their catchment basins. The strongly permeable sandy substratum of the catchment basins of the reservoirs at Przeczyce and Kozłowa Góra favour a higher content of manganese in the water. The largest amount of copper was noted in the water of the reservoir at Turawa, which receives mineral pollution. On the other hand, the water of the reservoir at Otmuchów, polluted chiefly with organic sewage, contained a relatively small amount of copper.

Finally, it is worth noting that during the same period, in the water of Goczałkowice reservoir, the primary production was determined (by the staff of the Laboratory of Water Biology of the Polish Academy of Sciences) and other trophic levels were investigated.

The author expresses his sincere thanks to Dr. E. Krzyżanek for collecting samples of water.

STRESZCZENIE

W opracowaniu przedstawiono wyniki badań nad zawartością i rozmieszczeniem (poziomym i pionowym) kilku ważniejszych mikroskładników (Cu, Zn, Mn) w wodzie zbiornika zaporowego w Goczałkowicach oraz zasilającej go rzece Wiśle (tabela II i III). W celach porównawczych podano w nim także uzyskane dane odnośnie do poziomu stężenia tych mikropierwiastków w czystych i zanieczyszczonych wodach siedmiu innych zbiorników zaporowych (tabela IV). Zawartość mikroskładników oznaczano w podkoncentrowanych roztworach metodą atomowej spektroskopii absorpcyjnej. W wodach wszystkich zbiorników badano równocześnie niektóre inne właściwości chemiczne (tabela II, III i IV).

Ilość poszczególnych badanych mikropierwiastków w wodzie rzeki Wisły i zbiornika goczałkowickiego wahała się w różnych zakresach. W wodzie rzeki najmniejszym wahaniom podlegała zawartość miedzi, a największym manganu. W wodzie zbiornika w najszerszych granicach zmieniała się ilość miedzi, a w najwęższych cynku. Dużą amplitudę wahań manganu w wodzie rzeki Wisły można tłumaczyć bardziej sprzyjającymi warunkami (większa zmienność temperatury, natlenienia) w rzece niż w zbiorniku dla fizyko-chemicznego wytrącania się go z wody oraz dopływem zanieczyszczeń i wód stawowych. Dość wyrównana ilość cynku w wodzie zbiornika wiąże się przypuszczalnie z kompensującym oddziaływaniem (sorpcją) substancji ilastych zawartych w dnie.

Przeciętna zawartość miedzi, cynku i manganu w wodzie zbiornika goczałkowickiego znacznie przewyższa ilości tych składników w czystych wodach badanych zbiorników karpackich (tabela II i IV). Jak się wydaje, jest to rezultatem pewnego stałego zanieczyszczania rzeki Wisły. Brak danych o zawartości mikropierwiastków w wodzie tej rzeki z okresu przed zalaniem zbiornika nie pozwala określić stopnia ilościowych zmian tych pierwiastków, jakie zachodzą w pewnym okresie czasu pod wpływem tychże zanieczyszczeń. Na podstawie uzyskanych danych można jedynie powiedzieć, że podwyższony poziom stężenia tych kilku mikropierwiastków w wodzie zbiornika stanowi ważny potencjalny czynnik pobudzający nadmierny rozwój glonów, który jest bardzo niekorzystnym zjawiskiem dla wodociągów. Prawdopodobieństwo masowych pojawów glonów w tym zbiorniku zwiększa dodatkowo jeszcze istnienie w nim stałej akumulacji mikroskładników oraz fakt przyspieszania ich ługowania z dna, na skutek dość silnego eolicznego mieszania wody. Jak bowiem zostało stwierdzone, więcej mikroskładników dopływa z wodą rzeki, niż odpływa. Średnia sezonowa zawartość miedzi, manganu i cynku w wodzie zbiornika goczałkowickiego jest również dużo wyższa od odpowiednich średnich ilości tych składników w czystych wodach wszystkich wymienionych w pracy zbiorników radzieckich.

Koncentracja mikropierwiastków w wodzie zbiornika goczałkowickiego wykazywała wyraźne poziome, pionowe i sezonowe zróżnicowanie. Rozpatrując poziomą zmienność ilości tych pierwiastków w wodzie zbiornika łącznie z rzeką, można powiedzieć, że przeciętnie najwięcej występowało ich w wodzie rzeki, nieco mniej w górnej części zbiornika, a najmniej w dolnej (ryc. 1). Pewien wyjątek stanowi

miedź, której w dwóch terminach było znacznie więcej w środkowej części zbiornika niż w górnej. Główną przyczyną tego, jak się wydaje, jest zahamowanie w tych terminach w wodzie środkowej strefy zbiornika fotosyntezy, na skutek obecności w niej w tym czasie sporej ilości zawiesin, które zostały poderwane z dna podczas silnego falowania. W pionowym przekroju wody zbiornika najmniejszą ilość wszystkich badanych mikroskładników notowano zwykle na głębokości około 1 m, a największą — w warstwie powierzchniowej i przydennej. Posługując się średnimi wartościami dochodzimy do wniosku, że w pionie wody najbardziej zmieniała się zawartość cynku (ryc. 2). Sezonowe zróżnicowanie zawartości mikropierwiastków w wodzie zbiornika goczałkowickiego wykazywało pewien związek z niektórymi ważniejszymi zjawiskami meteorologicznymi mającymi duże znaczenie dla rozwoju organizmów wodnych (ryc. 3, tabela I). Ogólnie biorąc, stosunkowo więcej mikroskładników występowało w wodzie tego zbiornika w mało usłonecznionych, deszczowych lub chłodnych okresach niż słonecznych i ciepłych.

Wszystkie odnotowane zróżnicowania zawartości mikroskładników w wodzie zbiornika w Goczałkowicach nie wykazywały, z małymi wyjątkami, wyraźnej zależności od innych badanych właściwości chemicznych wód. Zróżnicowania te wiążą się raczej, jak wskazują niektóre stwierdzone dane (pionowa zmienność i zależność sezonowego zróżniowania od czynników meteorologicznych), z nasileniem rozwoju glonów wodnych oraz dopływem zanieczyszczeń.

Zanieczyszczenia wyjątkowo mocno rzutują na podwyższenie w wodach badanych zbiorników zawartości cynku i manganu (tabela IV). Występowanie manganu w wodach zbiorników zależy ponadto także w dużej mierze od charakteru podłoża ich zlewni. Dobrze przesiąkliwe piaszczyste podłoże zlewni zbiorników w Przeczycach i Kozłowej Górze sprzyjają większej zawartości manganu w wodzie. Największą ilość miedzi stwierdzono w wodzie zbiornika w Turawie, który otrzymuje zanieczyszczenia mineralne. Stosunkowo mało miedzi zawierała natomiast woda zbiornika w Otmuchowie, który zanieczyszczany jest głównie ściekami organicznymi.

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