

KAZIMIERZ PASTERNAK

**Wstępne badania nad właściwościami
drobnych powierzchniowych osadów dennych rzeki Raby**

**Preliminary investigations on the properties
of fine surface bottom sediments of the River Raba**

Wpłynęło 14 października 1968 r.

Abstract — The paper reports the results of investigations of fine surface sediments of the Carpathian river Raba. The sediments were collected in various sections of the river during a period of sunny weather and after rainfall, as soon as the turbid water had flowed down. At the points of collecting the sediments the chemical composition of the river water was analysed in the course of each sampling. The grain composition, the reaction, the content of carbon, of total nitrogen, and of freely soluble phosphorus were determined in the sediments. A complete chemical analysis of the part of sediments soluble in 20 per cent HCl was carried out. On the basis of the physicochemical differentiation of the sediments in the longitudinal profile of the river and of the chemical composition of its water conclusions were drawn concerning the variability of the productivity of the river in its particular sections.

In a river bed, in spite of the continuous transportation, there occurs a deposition not only of the dragged and part of the carried away rock debris washed down from the catchment basin, but also of a certain amount of mineral salts precipitated from the water, and of remains of aquatic organisms. The quality and quantity of these debris stored in the river depend on a number of factors, but chiefly on the velocity of the flow of water in the river and on the morphology and character of the catchment basin (Burz 1958, Kajetanowicz 1958, Glenn and Dahl 1959). On the other hand, the quantity and properties of fine surface bottom sediments of the river are in great measure conditioned by the degree of settling of aquatic organisms, especially of plant organisms. A knowledge of the character and variability of these sediments may therefore throw some light on the productivity of the river. Data

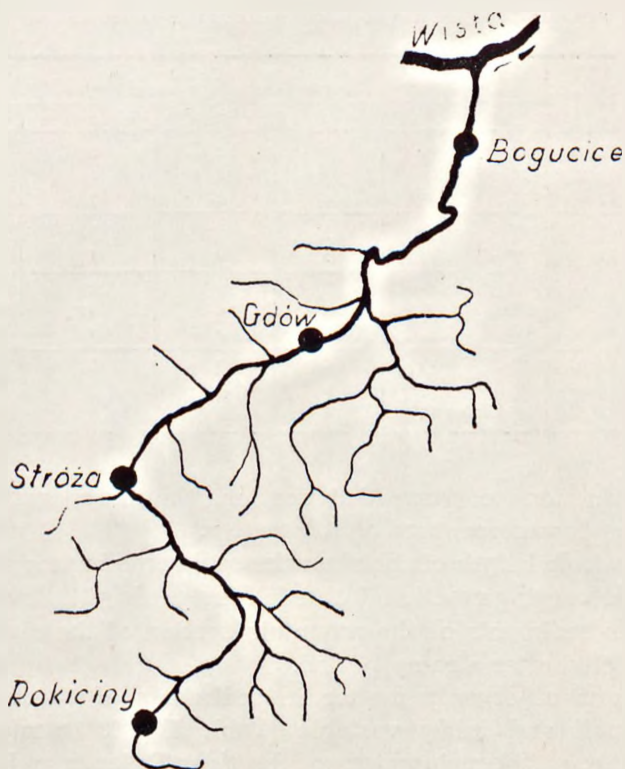
concerning the properties of these sediments are rather scarce in the literature, apart from those found in the works of D r o v e r and B e s h a i (1962) and M a j s t r e n k o (1965), who dealt more widely with this subject. But particularly little is known about the quality and variability of this kind of sediments occurring in the rivers of Poland.

In this connection, within the framework of complex investigations of the Carpathian river Raba, carried out by the Laboratory of Water Biology of the Polish Academy of Sciences in Cracow, investigations were undertaken aimed at determining the physicochemical properties of fine sediments of this river. The results obtained are reported in the present publication.

Method of investigations

Fine sediments are deposited on the bottom of mountain rivers of strong current only in the larger depressions of the bottom between stones and usually in shallow quiet places near the banks. Hence, it was only from these places that the examined sediments of the mountain part of the river were collected. The points of sampling the sediments in the longitudinal profile of the river are shown in fig. 1. Average samples of the sediments were collected to the amount of 1 dcm³ in cross-sections of the river over a section of about 50 m. Two sampling points were localized in the mountain course of the river, the lower one at Stróza at an exceptionally swift and shallow quiet place. One point was set in the transitional (Gdów) zone of the river, another in its level (Bogucice) zone with deeper and slower flowing water. The bed of the river Raba is stony in the mountain section, stony and sandy in the transitional one, and sandy for the most part in the level section. The character of the structure of this bed was described by the author in another study (P a s t e r n a k 1969). The sediments were collected twice during a period of sunny weather in the summer and autumn of 1967, and once in the spring of 1968 after a rainy period and with a somewhat raised water level in the river, when the water had become clear again. Before analysis the sediments were dried in the open air. The chemical composition of the river water was examined each time at the points of sampling the sediments.

The grain composition of the sediments was determined according to the C a s a g r a n d e - P r ó s z y ŋ s k i method, the carbon content with the A l t e n method, the total nitrogen according to K j e l d a h l, the reaction electrometrically, and the content of freely soluble phosphorus with the W o n d r a u s c h method. Potassium and sodium in an extract of 20 per cent HCl were determined with a flicker photometer, the other constituents in weight per cent or colorimetrically, according to the



Ryc. 1. Rozmieszczenie stanowisk badawczych na rzece Rabe

Fig. 1. Distribution of the points of sampling sediments in the river Raba

principles of the analysis of silicates. The chemical composition of water was analysed with the Just and Hermanowicz (1964) method and by Standard Methods (1955).

Results of investigations

The grain composition of fine bottom sediments of the river Raba corresponds in all the investigated points to that of loose sands with a relatively little varying percentage of the colloidal clay fraction (Table I). A markedly larger amount of clayey matter was found only in the sediments collected in the autumn of 1967 at the mountain point at Stróża. Apart from this single case, there also appeared a slight difference in the amount of colloidal matter ($< 0,002$) between sediments from one sampling point, collected at various terms. It is worthy of note is that these finest particles concentrate on the bottom of the river chiefly on the surface of the sandy sediment in the form of a very thin coating.

Tabela I. Skład mechaniczny osadów dennych rzeki Raby w %

Table I. Mechanical composition of bottom sediments in the river Raba in %

Miejscowość Locality	Data Date	Średnica cząstek gliny w mm Particle diameter in mm						Suma Total < 0,02
		1-0.1	0.1-0.05	0.05-0.02	0.02-0.006	0.006-0.002	< 0.002	
Bogucice	30 VI 67	72	14	7	2	2	3	7
	17 X 67	80	11	3	2	1	3	6
	7 VI 68	86	4	4	2	1	3	6
Gdów	17 X 67	73	15	3	4	1	4	9
	7 VI 68	85	5	3	2	1	4	7
Stróża	30 VI 67	83	4	5	3	2	3	8
	17 X 67	70	9	6	6	4	5	15
	7 VI 68	81	5	6	2	1	5	8
Rokiciny	30 VI 67	73	13	6	3	2	3	8
	17 X 67	80	9	6	0	3	2	5
	7 VI 68	75	11	6	2	1	5	8

In contradistinction to suspended matter, the investigated sediments contain a very low percentage of silt matter.

Over the whole length of the river the sediments have a weak-alkaline and very little varying reaction (Table II). Insignificantly lower pH values were noted in sediments of the mountain section of the river, especially in those collected after a rainy period.

The amount of organic matter in sediments of the river Raba is relatively small and fairly variable (Table II). It is much larger in sediments of, e. g., the rich waters of the river Dnieper and its affluents, and in those of the polluted waters of the Danube (Majstrenko 1965). The differentiation in the amount of organic matter in sediments of the river Raba is marked both as regards the time of sampling and the point of collecting the sample. Richest in organic matter are generally sediments collected in the middle of the summer. In late autumn sediments the content of organic matter is smaller, being the least after the flowing down of the river's turbid waters. As concerns the differentiation of organic matter in sediments along the course of the river, a higher content is noted at all terms in the upper section of the river (similarly as in the river Dnieper). The least variability of sediments with regard to the content of organic matter in the longitudinal profile of the river is marked after a period of occurrence of turbid water in the river.

The investigated sediments are characterized by a very narrow C : N ratio, varying within the range 6.82 to 11.43 (Table II). A similarly narrow C : N ratio is noted in sediments of the pure tributaries of the river Dnieper, whereas in sediments of the Danube this ratio is much larger (Majstrenko 1965). The narrow C : N ratio in sediments of the river Raba supports the hypothesis that the principal source of organic matter occurring in them are algae, in which, according to

Mira (1938), the C:N ratio is about 6. It may be that the narrow ratio of nitrogen to carbon is also related to the alkaline reaction of the sediments, for, as was established by Nömmik and Nilsson (1963), the bonding of ammonia by colloids increases in an alkaline medium. Taken as a whole, the sediments of the White Nile also contain large quantities of nitrogen (Drover and Beshai 1962). Of all points in which the sediments were examined the largest C:N ratio (9.58—11.43) was observed in sediments of the source section of the river, of stream character (Rokiciny). It seems that this is due to the somewhat greater possibility of a direct inflow to the bottom of a small trickle of allochthonous organic matter with a lower nitrogen content, proceeding from trees growing fairly thickly in this section on the parts nearest the banks.

Tabela II. Zawartość substancji organicznych, organicznego węgla, całkowitego azotu, łatwo rozpuszczalnego fosforu oraz odczyn osadów dennych rzeki Raby

Table II. The content of organic substances organic carbon, total nitrogen, available phosphorus and the reaction of bottom sediments in the river Raba

Miejscowość Locality	Data Date	Substancja organiczna Organic substance	C %	N %	C:N	P ₂ O ₅ mg/100 g osadu of sediment	pH (in H ₂ O)
Bogulice	30 VI 67	0.59	0.34	0.039	8.72	4.7	7.40
	17 X 67	0.31	0.18	0.026	6.92	4.5	7.45
	7 VI 68	0.26	0.15	0.020	7.50	3.0	7.55
Gdów	17 X 67	0.72	0.42	0.046	9.13	3.7	7.40
	7 VI 68	0.31	0.18	0.024	7.58	4.5	7.50
Stróża	30 VI 67	0.79	0.46	0.061	7.54	4.0	7.35
	17 X 67	1.03	0.60	0.088	6.82	5.0	7.30
	7 VI 68	0.55	0.32	0.041	7.80	3.5	7.15
Rokiciny	30 VI 67	1.10	0.64	0.056	11.43	3.8	7.40
	17 X 67	0.79	0.46	0.048	9.58	3.5	7.35
	7 VI 68	0.62	0.36	0.036	10.00	7.0	7.15

The chemical composition of sediments is differentiated along the course of the river, similarly as in the case of organic matter (Table III). On the whole, the least chemical constituents soluble in 20 per cent HCl are found in sediments of the level section of the river. The sediments of the submontane section contain a somewhat larger amount of these constituents, the largest being noted in sediments of the mountain section, especially at the point situated in a shallow quiet place of the river at Stróża. These differences are chiefly due to the different content of calcium, magnesium, colloidal silica, iron, and phosphorus (total) in these sections of the river. Sediments of its mountain section collected during a period of sunny weather sometimes contain a several times larger quantity of calcium than those of the lower section. On the whole, the sandy sediments of the river Raba contain a fairly large quantity of

calcium. Taking into account all times of sampling, their content of this element at the two lower points of the river amounts to 0.30—0.58 weight-% CaO, and in the upper ones to 0.72—2.28 per cent. For comparison it is worth noting that in the White Nile the content of calcium in sediments lies within the range 0.3 to 8.8 per cent (Drover and Desh ai 1962). The quantitative distribution of calcium along the course of this river is the reverse of that in the Raba (different climate, hydrology, and differentiation of the quality of the substratum in the catchment basin). The content of potassium in the sediments of the river Raba is in principle very much the same at all the investigated points, being fairly high for a loose sand. It is only in the level course of the river that the sediments contain much less of this component. Sodium in the particular sections of the river occurs in the sediments in small, and similarly as in the case of potassium, little variable quantities. Its content

Tabela III. Skład chemiczny rozpuszczonej w 20 % HCl części osadów dennych rzeki Raby (powietrznie suchego osadu) (SiO₂ uruchamiano 5 % Na₂CO₃)

Table III. ¹ Chemical composition of the 20 % HCl - soluble part of bottom sediments in the River Raba (air-dry sediments) (SiO₂ was activated with 5 % Na₂CO₃)

Miejscowość Locality	Bogucice			Gdów		Stroża			Rokiciny		
	30 VI 1967	17 X 1967	7 VI 1968	17 X 1967	7 VI 1968	30 VI 1967	17 X 1967	7 VI 1968	30 VI 1967	17 X 1967	7 VI 1968
SiO ₂	2.42	1.75	1.66	2.68	2.58	3.76	4.46	3.06	2.83	2.75	2.66
P ₂ O ₅	0.05	0.03	0.03	0.04	0.03	0.07	0.04	0.04	0.07	0.05	0.06
Al ₂ O ₃	1.32	0.98	0.82	1.68	1.28	1.86	2.65	1.79	1.64	1.65	1.53
Fe ₂ O ₃	1.50	0.98	1.13	1.90	1.61	2.18	2.85	2.00	1.68	1.57	1.53
MnO	0.03	0.03	0.03	0.03	0.02	0.04	0.06	0.05	0.03	0.03	0.03
CaO	0.51	0.30	0.38	0.58	0.43	2.28	2.26	0.72	0.89	1.26	0.86
MgO	0.42	0.30	0.34	0.50	0.36	0.58	0.77	0.59	0.65	0.58	0.67
K ₂ O	0.25	0.21	0.20	0.31	0.26	0.30	0.38	0.28	0.26	0.29	0.24
Na ₂ O	0.09	0.13	0.10	0.14	0.10	0.08	0.16	0.09	0.07	0.13	0.09
SO ₃	0.08	0.10	0.07	0.11	0.07	0.10	0.13	0.07	0.07	0.12	0.07
Suma części rozpuszczalnych w HCl Total of soluble parts in HCl	6.67	4.81	4.76	7.97	6.74	11.25	13.76	8.69	8.19	8.43	7.74
H ₂ O 105°C	0.55	0.25	0.20	0.44	0.24	0.56	0.60	0.31	0.58	0.44	0.29
Strata tarowa Loss in ignition	1.87	0.96	0.75	2.13	1.02	3.66	3.90	1.45	2.84	2.82	1.51
Suma części nierozpuszczalnych w HCl Total of insoluble parts in HCl	91.02	94.00	94.45	89.52	92.14	84.57	81.89	89.68	88.48	88.36	90.65
Suma Total	100.11	100.02	100.16	100.06	100.14	100.04	100.15	100.13	100.09	100.05	100.19

Tablica IV. Fizyko-chemiczne właściwości wody rzeki Raby
 Table IV. Physico-chemical properties of water in the River Raba

Locality Miejscowość	Date	Temperature of water Temperatura of water °C	Oxygen Tlen rozpuszczony O ₂ mg/l	Oxygen saturation Uygień nasycenia tlenu %	Free carbon dioxide Wolny dwutlenek węgla CO ₂ mg/l	pH	Alkalinity me.	Hardness ogólna in German °d Twardość ogólna w Niemczech °d	Hardness Ca mg/l Twardość Ca mg/l	Magnesium Magnez mg/l	Potassium Potas K mg/l	Sodium Sód Na mg/l	Iron Żelazo Fe mg/l	Chloride Chlorki Cl mg/l	Sulphate Siarczany SO ₄ mg/l	Phosphate Fosforany PO ₄ mg/l	Ultraviolet Ultrafiolet U ₂ mg/l
Bogucice	30.VI.1967	20,5	8,48	93,2	3,1	7,9	3,0	10,1	56,5	9,5	2,84	10,16	0,06	12,0	36,9	trace	6,4
	17.X.1967	14,4	9,28	90,0	1,4	7,9	2,8	9,3	49,3	10,2	2,59	11,00	0,07	12,5	34,6	SI. trace	2,2
	7.VI.1968	21,4	8,48	94,7	2,6	8,0	2,6	9,1	48,6	10,0	1,96	8,48	0,08	9,8	36,5	0,01	2,7
Gdów	17.X.1967	15,0	11,68	114,7	0,5	8,2	2,7	9,2	45,7	12,1	2,19	7,44	0,02	7,5	35,5	SI. trace	2,0
	7.VI.1968	23,5	9,92	115,3	1,0	8,2	2,4	8,1	42,5	9,3	1,75	6,24	0,04	6,8	27,4	SI. trace	2,3
	30.VI.1967	24,0	10,40	122,1	0,0	8,4	2,5	7,9	42,9	8,2	2,20	5,12	0,00	5,5	21,1	0,01	2,7
Stróża	17.X.1967	16,4	12,00	121,3	0,0	8,5	2,5	8,0	42,5	8,9	2,09	6,40	0,00	6,3	24,0	0,01	1,7
	7.VI.1968	23,1	10,0	115,5	0,0	8,6	2,4	8,0	42,2	9,3	1,49	5,08	0,02	5,3	25,0	SI. trace	2,3
Rożcizny	30.VI.1967	23,2	8,64	100,1	0,0	8,2	2,9	9,4	51,5	9,5	2,00	4,96	0,02	6,0	26,4	SI. trace	5,7
	17.X.1967	15,3	9,28	91,7	0,0	8,4	2,8	8,9	46,5	10,4	1,89	5,80	0,03	7,2	24,0	0,01	2,5
	7.VI.1968	21,1	8,48	94,2	0,0	8,2	2,6	8,9	47,9	9,5	1,39	4,48	0,03	6,0	27,8	SI. trace	3,8

is the lowest in sediments of the source section of the river. Manganese occurs in the sediments in relatively large (for a sandy deposit) and mostly equal quantities. A regularly higher content of this component was noted only in sediments at the mountain sampling-point of Stróža. A generally lower content of components soluble in 20 per cent HCl was found in sediments collected after a period of turbid water in the river. It should be stressed that the chemical composition of sediments from this period is little differentiated along the course of the river, especially in regard to the amount of basic constituents. An interesting trait of the investigated sediments is their exceptionally high content of iron in relation to the mechanical composition. Moreover, this constituent in most cases prevails quantitatively over aluminium, this being a rather infrequent phenomenon. Worthy of note also is the fact that at all sampling points and terms the sediments contained a relatively small quantity of sulphates (Table III) and a fairly large one of freely soluble phosphorus (Table II). The content of the latter in the sediments varied little in the particular sections of the river.

The water of the river Raba at all points of sampling the sediments and at the various terms was like every pure mountain river well saturated with oxygen (Table IV). A particularly high O₂ content was noted in the water at the Stróža sampling-point. As compared with the water of the lower and transitional section of the river the water in its mountain course contained no free CO₂ or phosphates at all and had a more alkaline reaction. Such a considerable saturation of water with oxygen in the upper course of the river is probably connected not so much with the increased contact of its water with air on the numerous cascades (spattering), than to the considerable development in it of plant organisms in the quiet places well exposed to the sun's rays and strongly heated by radiation. According to the existing opinion, periphyton, for example, has the ability of storing oxygen in its coatings and can supply water with it even beyond the time of assimilation (S t a r m a c h 1963). In contradistinction to the lower section of the river, in the water of its mountain section strongly saturated with oxygen and containing no free CO₂, a disappearance or minimum quantities of iron were noted. Moreover, at the sampling-point in Stróža the general hardness of the water was regularly lower than in the source section. The oxidability of water in the whole course of the river was generally small and little differentiated.

Discussion and conclusions

A comparison of the numerical data obtained shows that the grain composition of sediments does not in most cases reflect their chemical

composition. The content of some elements in the sediments is much higher than in the washed alluvial fluvio-glacial loose sandy deposits of other environments (Pasternak 1967). This refers particularly to calcium and iron.

With the advancing course of the river the chemical composition of sediments becomes more and more differentiated. The greatest quantities of calcium, magnesium, iron, phosphorus soluble in 20 per cent HCl, colloidal silica, and sometimes of manganese occur in sediments of the mountain section of the river. The content of these components is lower in sediments of the submontane region, being lowest in those from the level region. A remarkably large quantity of calcium and iron occurs in sediments collected in the shallow zone of the river with quiet places. Analogously larger quantities of calcium occurred in sediments in the quiet places of the White Nile (Drover and Beshai 1962).

The chemical differentiation presented above of sediments along the course of the river Raba also fails in most cases to correspond to the changes of their mechanical composition. Nor is the chemical variability of bottom sediments in the longitudinal profile of this river justified by the structure and quality of the substratum of its catchment basin (Pasternak 1969). The sediments of the mountain section of the river are also richer in organic matter than those from its lower course. It seems, therefore, that the differentiation of chemical properties of fine sediments along the course of the river Raba is chiefly due to the different intensity in its particular sections of the processes of deposition of organic matter and mineral salts from the aquatic environment. This opinion is supported by the fact that the sediments of the river after a period of occurrence of turbid water in it (sweeping away of organisms, weaker photosynthesis), in spite of the necessity of collecting them only after the water had become quite clear, are poorer in organic and basic mineral compounds and their chemical composition is more uniform on the whole length of the river. Another argument supporting this opinion is the presence in the sediments of organic matter of a C:N ratio approximate to that in algae.

The intensity of processes of precipitation from the river water of mineral salts and of the deposition on its bottom of organic matter chiefly depend (indirectly or directly) on the degree of development of various organisms in the aquatic environment of the river. The accumulation of some mineral salts and organic matter in fine surface sediments of the river, more intense in its mountain course than in the lower one, therefore indicates that the upper section of the river, especially that with quiet places, is characterized by a greater production than the lower one. This is corroborated by the chemical composition of water only at the site at Stróža. The water at that point of the river, in spite of the usually strong current and rapid renewal of its mass, was as a rule the most

oversaturated with oxygen, contained no free CO_2 , and had the highest pH. To learn what is the actual production of the river Raba further investigations must be carried out, being particularly concerned with the production of bottom algae and periphyton.

STRESZCZENIE

W pracy przedstawiono wyniki badań nad fizyko-chemicznymi właściwościami drobnych powierzchniowych osadów karpackiej rzeki Raby. Osady pobierane były w różnych odcinkach rzeki (średnie próby z 50 m odcinka) podczas ustalonej słonecznej pogody oraz po opadach deszczu zaraz po spłynięciu mętnej wody. W miejscach pobierania osadów (ryc. 1, 2) każdorazowo analizowano skład chemiczny wody rzeki.

Drobne osady rzeki Raby mają we wszystkich badanych punktach skład granulometryczny odpowiadający piaskom luźnym o stosunkowo mało zmiennym procencie frakcji ilu koloidalnego (tabela I). Małe zróżnicowanie w ilości koloidalnych części ilastych, z wyjątkiem jednego przypadku, zachodzi także pomiędzy osadami z jednego stanowiska pobranymi w różnych terminach.

Na przestrzeni całej długości rzeki osady mają słabo alkaliczny i bardzo wyrównany odczyn (tabela II). Ilość substancji organicznych w osadach jest stosunkowo mała i dość zmienna (tabela II). Zróżnicowanie w ilości materii organicznej w osadach zaznacza się zarówno w odniesieniu do terminu, jak też punktu poboru próby (wzdłuż biegu rzeki). Na ogół najzasobniejsze w substancje organiczne są osady pobrane w środku lata. Mniejszą ich ilość mają osady późnojesienne, a najmniejszą po okresie występowania w rzece mętnej wody.

Osady górnego odcinka rzeki we wszystkich terminach zawierają więcej substancji organicznych niż osady jej dolnej części. Najmniejsza zmienność osadów pod względem zawartości materii organicznej w podłużnym profilu rzeki zaznacza się po okresie deszczowym (mętnej wody). Badane osady odznaczają się bardzo wąskim stosunkiem C : N. Przemawia to za tym, że głównym źródłem materii organicznej są glony, których stosunek C : N wynosi około 6. Być może, że wąski stosunek C : N wiąże się także z alkalicznym odczynem osadów. Większa w źródłowym odcinku możliwość dopływu allochtonicznej materii z brzegów powoduje poszerzenie stosunku C : N.

Skład chemiczny osadów różnicuje się wzdłuż biegu rzeki podobnie jak w przypadku materii organicznej (tabela III). W sumie najmniej składników chemicznych rozpuszczalnych w 20% HCl mają osady równinnego odcinka rzeki, nieco więcej podgórskiego, a najwięcej górskiego, zwłaszcza w punkcie na płytkim rozlewisku rzeki w Stróży. Różnice te wynikają głównie z odmiennej na tych odcinkach rzeki zawartości wapnia, magnezu, koloidalnej krzemionki, żelaza i fosforu (ogólnego).

Ogólnie mniejszą zawartość składników rozpuszczalnych w 20% HCl i mniejsze ilości zróżnicowanie wzdłuż biegu rzeki mają osady po okresie występowania mętnej wody. Osady, jak na luźny piaszczysty utwór, zawierają wyjątkowo dużo żelaza i manganu.

Woda górskiego biegu rzeki, w odróżnieniu od dolnego, miała największe przeżyty tlenowe i bardziej alkaliczny odczyn oraz nie zawierała w ogóle wolnego CO_2 i fosforanów (tabela IV). Na stanowisku w Stróży woda rzeki odznaczała się ponadto stale mniejszą niż w źródłowym odcinku twardością ogólną.

Z zebranych danych wynika, że chemizm osadów, w większości przypadków, nie jest odzwierciedleniem ich składu granulometrycznego. Zmienność chemiczna

osadów dennych w profilu podłużnym rzeki nie znajduje też uzasadnienia w budowie i jakości podłoża jej zlewni. Wydaje się więc, że przyczyna zróżnicowania chemicznych właściwości drobnych osadów wzdłuż biegu rzeki Raby tkwi przede wszystkim w odmiennym nasileniu, na poszczególnych jej odcinkach, procesów odkładania ze środowiska wodnego materii organicznej i soli mineralnych. Wskazuje na to także mniejszy zasób organicznych i mineralnych związków zasadowych w osadach pobranych po okresie deszczów oraz bardziej wyrównany wtedy chemizm tych osadów na całej długości rzeki.

Intensywniejsza w górskim niż w dolnym biegu rzeki akumulacja niektórych soli mineralnych i substancji organicznych w drobnych osadach rzeki wskazuje, że górny odcinek rzeki odznacza się większą produkcją niż dolny. W chemizmie wody potwierdza się to wyraźnie jedynie na stanowisku w Stróży.

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Adres autora — Author's address

doc. dr Kazimierz Pasternak

Zakład Biologii Wód, Polska Akademia Nauk, Kraków, ul. Sławkowska 17.