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The effect of nitrogen fertilization of bankside soils on the chemical characteristics of the River Nida (Southern Poland) with special regard to dissolved organic matter*

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Abstract — Fertilization with ammonium nitrate at doses of 80 kg per 1 ha experimental meadow minimally affected the content of dissolved protein and dissolved organic matter. This was manifested only in spring and autumn, when the concentrations of dissolved protein were in increasing order from the control station located 300 m above the experimental meadow to one situated 200 m below the central station.

Key words: rivers, nitrogen fertilization, dissolved organic matter, dissolved protein, seasonal changes.

1. Introduction

Mineral fertilization is a general practice in agriculture. Ammonia nitrogen introduced with fertilizers into the soil is to a marked degree absorbed by it and may also be oxidized by bacteria to nitrates. The latter form originates either from the conversion of ammonia nitrogen or directly from the fertilizers (saltpeter) and, being soluble, passes to the soil solution (Gorlach 1979). If not utilized by crop plants, it enriches flowing waters, bringing about the numerous development of phytoplankton and vascular plants. This is particularly dangerous in slowly flowing lowland rivers where the transport of organic matter is sluggish. On account of the eutrophication brought about by the excessive production of organic matter, the normal functioning of the river ecosystem may be disturbed (Mańczak 1979, Wróbel 1981).

The aim of the present work was to investigated the effect of fertilization of a meadow lying in the direct vicinity of the River Nida on the

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chemical properties of the water, especially the concentration of dissolved organic matter in the form of both organic C and albumin. In the aspect of fertilization the results are a contribution to the complex study carried out in the River Nida (Kawecka 1986, Starzecka, Mazurkiewicz 1987, Bombówna unpubl., Grabacka unpubl.).

2. Study area

The investigation was carried out at montly intervals in the period July 1983 — May 1985. In the first year six stations (1, 2, 3, 4_1, 4_2, 4_3) on the Nida were investigated while in the second at most sampling dates only three stations (4_1, 4_2, 4_3) were taken into consideration (fig. 1).

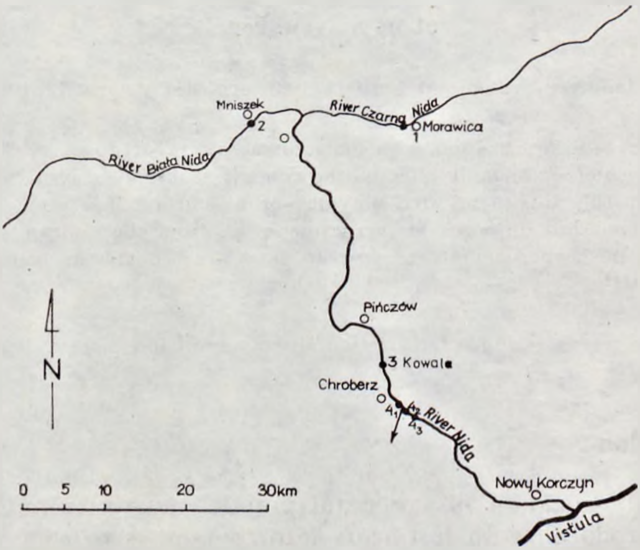

Fig. 1. Map of the investigated stations on the River Nida. 1—4_3 — stations. Locality of the experimental meadow is marked by a arrow

The upper Station 1 was situated at Morawica on the River Czarna Nida flowing out of the paleozoic quartz massif of the Świętokrzyskie Mts. Station 2, also an upper one, lay on the River Biała Nida whose springs were found in the Jędrzejów tableland, rich in cretaceous rocks (Kostrowicki 1957). The station was established at Mniszek in wet peaty terrain. Further stations lay in the lower river course of the Nida, i.e., Station 3 at Kowala below the town of Pińczów, and the next three at Chroberz. The first control station (4_1) was established at a distance of 300 m above the experimental meadow in the Nida meander where shallows occurred. The next station (4_2) lay 100 m lower, just opposite

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the experimental 1 ha meadow, fertilized with ammonium nitrate (NH_4NO_3) in 3 doses of 80 kg N ha^{-1} each on the following dates: June 15 and September 10, 1983; April 18, July 7, and September 6, 1984; and April 12, 1985. The third station (4_3) lay at a distance of 200 m from the middle one. The two last stations had a more uniform bank line than the control station, while the riverbed was of approximately even depth.

3. Material and methods

On all dates the river water for analyses was sampled from the current and on May 13, 1985 also from the part near the bank. Water samples were transported to the laboratory and stored in a refrigerator. Chemical analyses of the water included the basic parameters, i.e., dissolved oxygen, BOD_5, oxidability, conductivity, and turbidity. Total residue and loss of ignition were also determined. Moreover, such biogenic components as nitrates, nitrites, ammonia and phosphates were taken into consideration. The generally accepted methods of analyses according to Hermanowicz et al. (1976), Golterman (1969), and Standard Methods (1971) were used in the work. In the present paper the mean values of the physico-chemical parameters mentioned above and their coefficients of variation were given, characterizing the general condition of the environment of the River Nida (Bombówna, unpublished data).

The hydrochemical investigation was supplemented by analyses of dissolved organic matter. Water samples were filtered through GFC Whatman glass microfibre paper and C-org mg dm^{-3} (dissolved organic matter, DOM) was spectrophotometrically determined, using a 1 cm quartz cell, at 360 μm wave length, according to the method described by Lewis and Canfield (1977). Dissolved protein (DP) was colorimetrically determined, using the Lowry-Folin method (Lowry et al. 1951) with Fluke AG albumine bovine cryst., used as standard.

In computing DOM and DP outflows data on surface run-off supplied by the Kraków Division of the Institute of Meteorology and Water Economy were used.

4. Results

The mean concentrations of particular components and the corresponding percentage coeficients of variability for the entire period of the investigation are presented in Table I.

The water from the upper stations, particularly Station 1, showed a poorer content of such nutrients as phosphates, nitrates, nitrites, and ammonia than the lower stations.

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Table 1. Some chemical factors of the River Nida from 17 July 1983 to 13 May 1985. $\bar{x}$ - mean value; V% - coefficient of variation (according to Bombowna unpubl.)

Factors \ Stations		1		2		3		4_1		4_2		4_3	
		$\bar{x}$	V%	$\bar{x}$	V%	$\bar{x}$	V%	$\bar{x}$	V%	$\bar{x}$	V%	$\bar{x}$	V%
Turbidity	mg SiO_2 dm^{-3}	21.6	114	20.30	46	31.80	48	37.70	54	40.80	55	35.50	41
Conductivity	µS 18°C	275.4	10	355.0	14	415.7	15	422.5	10	[illegible]	11	427.0	11
Dissolved oxygen	mg O_2 dm^{-3}	11.2	12	10.7	19	8.4	41	7.8	29	7.6	39	7.0	39
Oxidability	mg O_2 dm^{-3}	5.2	29	8.7	25	7.2	23	7.0	14	7.4	18	7.5	18
BOD_5	mg O_2 dm^{-3}	2.7	74	5.4	76	4.8	28	5.3	33	5.9	36	5.9	35
Total residue	mg dm^{-3}	221.5	6	270.9	7	339.2	9	368.9	5	370.6	7	368.8	7
Loss of ignition	mg dm^{-3}	74.7	16	105.1	7	92.7	28	115.2	21	[illegible]	20	108.6	21
Ammonium	mg $N-NH_4$ dm^{-3}	0.296	14	0.416	13	1.047	55	1.240	67	1.230	66	1.370	58
Nitrate	mg $N-NO_3$ dm^{-3}	0.890	71	0.528	64	1.030	50	1.100	42	1.150	37	1.180	35
Nitrite	mg $N-NO_2$ dm^{-3}	0.007	47	0.009	47	0.061	67	0.055	77	0.061	84	0.082	65
Phosphate	mg $P-PO_4$ dm^{-3}	0.060	48	0.160	29	1.059	24	1.130	39	1.053	49	1.179	39

A reverse situation was found with regard to dissolved oxygen, the largest content of which appeared at the two upper stations (1 and 2). At the successive stations down river this content was observed to decrease. A great variation in the content of dissolved oxygen appeared at Station 3 and at Stations 4_2 and 4_3, lying within the range of the fertilization experiment; at the remaining stations the variation was only slightly smaller.

The lowest mean concentration of oxidability occurred at Station 1 and the highest at Station 2. The highest coefficient of variation of this parameter was found at Station 1. From Station 2 it decreased in the following order of stations: 2, 3, 4_2, 4_3, and 4_1.

The lowest value of BOD_5 as the index of concentration of biochemically decomposable organic matter was found at Station 1. At the remaining stations this factor did not greatly change. A fairly great variation of BOD_5 was noted at Stations 1, 2, and 3 while at the remaining stations it was almost half that found at Station 1.

The highest concentration of turbidity appeared at Station 4_2, directly associated with the fertilization, and slightly lower ones at Station 4_1 (control) and 4_3 (200 m below the experimental meadow). At Stations 1 and 2 the turbidity was half the maximum value of that found at Station 4_2. The greatest variation of this component appeared at Station 1, while at the remaining sampling stations the coefficient of variation was reduced almost by half.

Like as turbidity, also conductivity showed the lowest value at the upper stations (1 and 2). At the remaining stations it was greater and similar. This parameter did not change much as was shown by the small range of the coefficient of variation.

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Total residue showed slightly lower values at the upper than at the lower stations. Of the parameters discussed this was the least variable.

The losses of ignition showed a similar pattern. The smallest variation of this parameter was found at Station 2, indicating the stability of organic matter there. This factor increased at the successive Stations from 1 to 4_3, with the exception of Station 2.

The concentration of ammonia greatly varied at the different stations. The value of this component was low at the upper Stations (1 and 2) and higher at the remaining ones. In increased down river, this indicating its eutrophication. The percentage coefficient of variation of this parameter suggested different dynamics in the processes of reduction of organic matter. The coefficient was very low at Stations 1 and 2, and higher by a few per cent and more varied at the other sampling points.

An analogous pattern of changes appeared in the mean content of nitrates and nitrites. Lower values of these components were found at the upper stations and higher ones down river. However, in the case of nitrites differences between these groups of stations were greater. The greatest range of variation in the content of nitrates was noted at Station 1; it decreased down the river course to Station 4_3, this probably suggesting the effect of fertilization. A reverse situation was observed in the case of nitrites. Great quantitative changes in the content of this component at the lower stations may indicate a greater microbiological activity of this river sector.

The mean content of phosphates increased similarly as that of nitrogen constituents, this also showing the pronounced eutrophication of the lower sector of the River Nida. However, the percentage coefficient of variation showed a different pattern from that nitrogen compounds. The smallest variations were observed at Stations 1 and 3. In the former case this was associated with the type of habitat, since organic matter from the wet marshy basin contained some amounts of humus compounds. They formed poorly decomposable complexes with phosphates, hence at Station 2 the content of phosphates did not greatly change. At Station 3 this was brought about by the constant inflow of industrial wastes from the neighbouring twon of Pińczów. The greatest variation in the con-

Table II. Different forms of organic matter in the River Nida from July 17, 1983 to May 13, 1985. $\bar{x}$ – mean value; V% – coefficient of variation

Factors	Data	Stations					
		1	2	3	4_1	4_2	4_3
C-org. dissolved mg dm^{-3}	$\bar{x}$	3.33	4.92	4.64	3.78	3.84	3.58
	V%	49	48	46	42	43	36
Protein dissolved mg albumine dm^{-3}	$\bar{x}$	2.22	3.87	3.03	3.72	3.45	3.86
	V%	32	49	35	45	40	39

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centration of phosphates was noted at Station 4_2, lying just opposite the experimental meadow, and at Station 1 in the upper river sector.

The content of dissolved organic matter (DOM) was little changed at the particular stations, as was shown by its mean concentrations (Table II). The smallest content appeared at the upper Station 1 and the largest at Station 2, also in the upper sector of the river. At Station 3 the content of this component was slightly smaller than at Station 2, while at the remaining stations intermediate values were found. However, in the case of Station 4_3 the difference in relation to the lowest concentration at Station 1 was small. The coefficient of variation of DOM varied from 36—49%. The highest coefficient was found at Station 1, a slightly lower one, but within the same range, at Stations 2 and 3, and the lowest one at Station 4_3. The rather small variation in the content of organic matter, particularly at Station 4_3, probably showed the intermediate action of fertilization. It supplied additional nutrients, which stimulated the production of phytoplankton biomass, the accumulation of organic matter being thereby favoured. It should be stressed that the

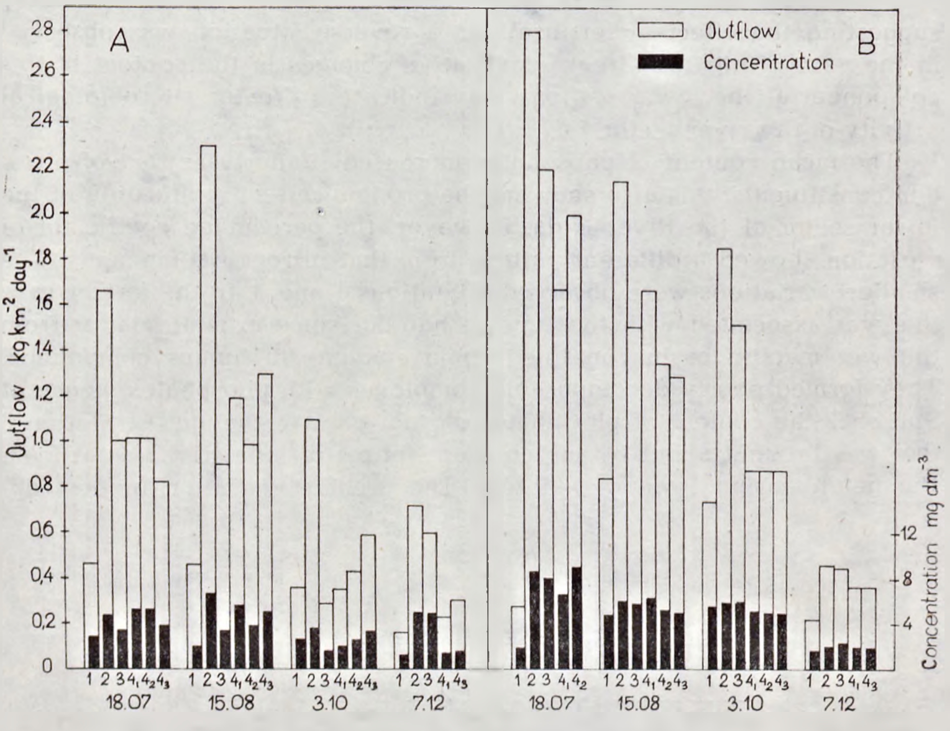

Fig. 2. The outflow and concentrations of A — dissolved protein in mg albumine dm^{-3}, and B — dissolved organic matter in mg C-org dm^{-3} in 1983 in the River Nida at Stations 1—4_3

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discussed coefficient was partly correlated with the coefficient of variation for oxidability (Tables I and II). The concentration of DOM depended in certain measure upon the season. In the first year of the study the maximum content of this component was recorded at almost all stations (with the exception of Station 1) in July and in the following year in August, while the smallest content appeared in the season of inhibited vegetation: in December 1983, November 1984, and in 1985, the last year of the experiment, at the beginning of March (figs 2B, 3B, 4B).

Changes in the content of dissolved protein (DP) were similar to those of DOM. The smallest content was found at Station 1 and the largest at Station 2. However, the concentrations of DP were slightly less stable than those of DOM. This was shown by the coefficient of variation within the range 32—49% (Table II). The content of DP in the River Nida also depended upon the season. In the first year of the study at most stations high concentrations were observed in July and August, with the exception of Station 4_2 where the content of this component was even reduced in August (fig. 2A). In the following year a tendency to increasing concentrations of DP already appeared in April. The maximum was noted in May at Station 4_2 and in June at Stations 4_1, and 4_3 (fig. 3A).

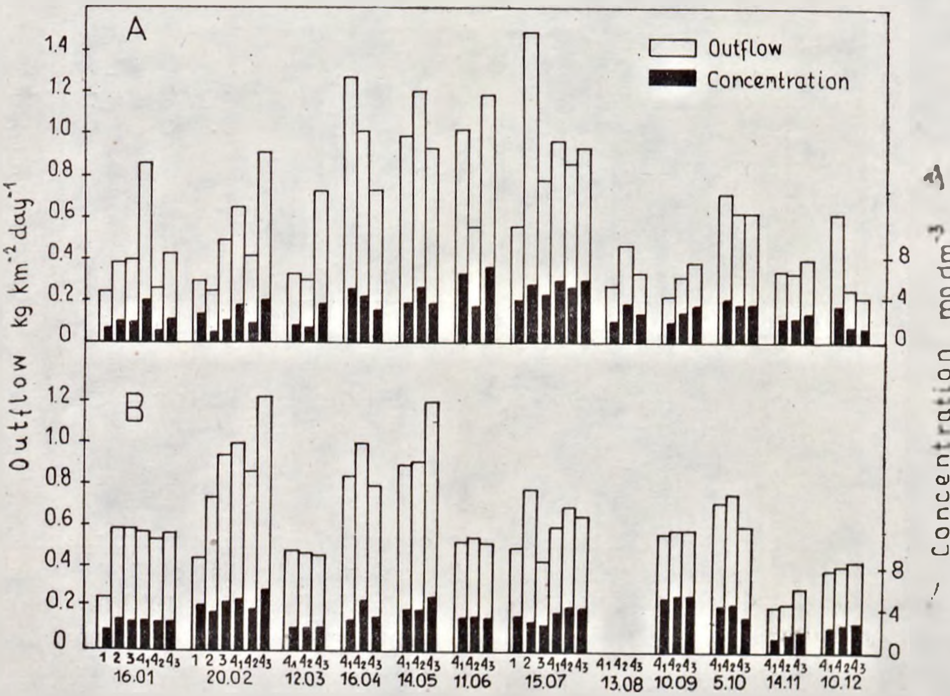

Fig. 3. The outflow and concentrations of A — dissolved protein and B — dissolved organic matter in 1984 in the River Nida at Stations 1—4_3

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In the last year of the study which covered the period January—May, an increase in the amount of dissolved protein already occurred in March, no variation being noted at the particular stations. The increase was brought about by the water flow which was double that noted in January. In March organic matter probably originated from fields, being washed off by melting snow but not produced in the river as was the case in the summer. In samples taken in April a distinct gradation of the

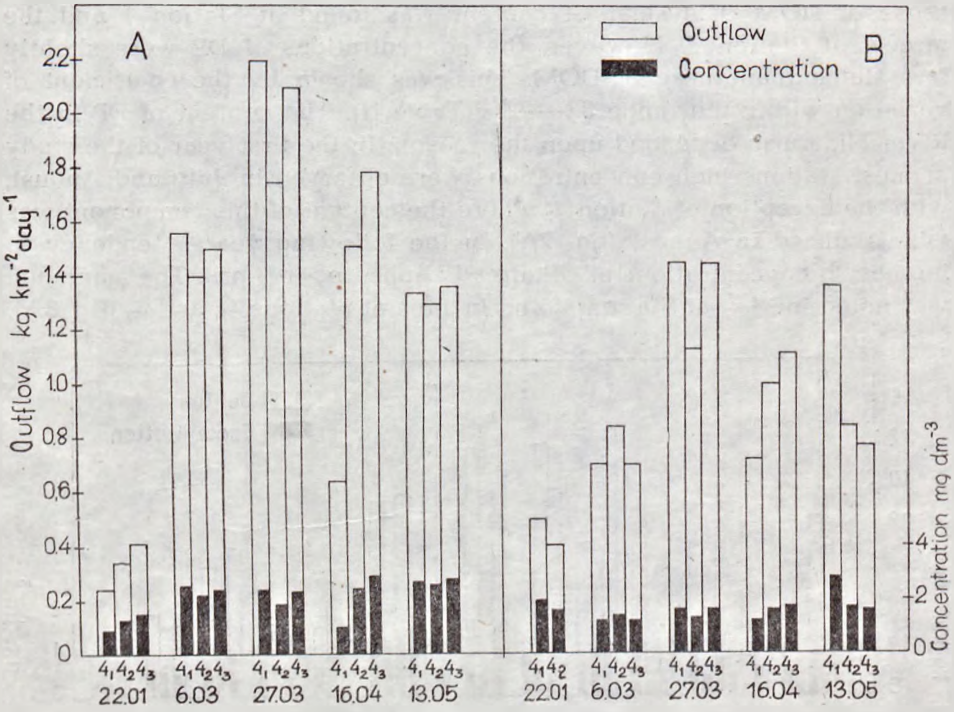

Fig. 4. The outflow and concentrations of A — dissolved protein and B — dissolved organic matter in 1985 in the River Nida at Stations 4_1—4_3

DP from Station 4_1 to Station 4_3 was observed. In the winter months a decrease in the concentration of DP, analogical to that of DOM, was usually observed. It fell at Stations 1, 4_1 and 4_3 in December 1983 (fig. 2A) and at the remaining stations as late as January 1984, with the exception of Station 4_1 where it even rose. The tendency to decreased concentrations of DP was also observed in November 1984 (fig. 3A) and this state was partly maintained in December and even in January 1985 (figs 3A, 4A).

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5. Discussion

In natural conditions the river ecosystems is affected by numerous interacting factors, among them hydrological, geological, and climatological ones and those associated with human activity. Therefore, it is difficult to define the effect of mineral fertilization on the chemical properties of river water, especially on the content of dissolved organic matter. In the River Nida the effect of this treatment was weakened both by the physiographic conditions and human activity. On account of the shape of the bank and the shallows associated with it, the control Station 4_1 offered more favourable conditions for the development of periphyton, and hence for increased primary production, than Stations 4_2 and 4_3. It probably brought about an increased content of DOM in this sector. Moreover, on account of the neighbouring town of Pińczów (food industry), the lower sector of the Nida, beginning from Station 3 at Chroberz, was to a great degree subject to eutrophication. This was shown by the larger amounts of biogenic components found in the water of the lower sector, probably unconnected with the fertilization experiment.

In lowland rivers, such as the Nida, a great role in the accumulation of particulate organic matter is also played by its transport from the basin. However, besides the allochthonous organic matter, a part of it is produced in the river with the participation of vascular plants, periphyton and seston. With the share of bacteria the particulate organic matter is mostly transformed in the dissolved form; nevertheless a part of the latter is an extracellular product of cells of lower and vascular plants (Wetzel, Manny 1972, Fogg 1966). Thus, on account of the more intense development of microorganisms, aquatic flora, and the surrounding habitats during the vegetation period, the concentration of the two forms of organic matter, DOM and DP, rose in relation to the early-spring, autumn, and winter seasons.

The effect of the fertilization on the content of DOM and DP was minimal in the early (spring) and final (autumn) part of the vegetation season. An almost model gradation, especially of DP, was obtained at that time. It was expressed by a successive quantitative increase from Station 4_1 to 4_3. DP is a more reliable index of biochemical conversions occurring in the river than DOM.

Apart from the factors discussed above, the effect of the fertilization could be more distinctly observed just after its application. This was shown by water samples from April 1985, taken 4 days after fertilization, at a decreased water flow of 1.66 $dm^3\ km^{-2}\ sec^{-1}$ as compared with the March sampling. The concentration of DOM, expressed as C-org, was less differentiated while that of DP gradually increased at the successive stations. At Station 4_2 it was double that at the control station,

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and at Station 4_3 it was even three times as great. On the other hand, in the water sampled still in the spring but one month after the fertilization (May 14, 1985) the rule that the content of organic matter rose when the distance from the control station increased, was not followed. Contrary to expectation, the content of DP was 1 mg greater at Station 4_2, opposite the meadow, than at Station 4_3 below the fertilized area.

Moreover, it was found that at a diminished water flow, i.e., when the transport of organic matter from the basin was eliminated, the state brought about by a local factor, in this case the fertilization, could be more easily observed. This was found in May when the water flow in the river was 1 dm^3 km^{-2} sec^{-1} slower than on the April sampling date. In May 1985 the samples of water were taken one month after the fertilization not only from the current but also from the part near the river bank. In the current the concentration of the two components of organic matter was almost uniform at all stations investigated, while in the water near the bank the situation was different. Owing to the sedimentation of organic matter, probably brought about the fertilization, the content of DP was 2 mg higher at Station 4_2 opposite the meadow and 3.5 mg dm^{-3} at Station 4_3 below the experimental area, compared with the control Station 4_1.

The action of mineral fertilizers was also manifested, though only in very small measure, in autumn samples both at the beginning of October 1983, 3 weeks after fertilization, and in 1984, 4 days after it. On these two sampling dates the surface run-off was small, reaching 1.91 dm^3 km^{-2} sec^{-1} and 1.28 dm^3 km^{-2} sec^{-1}, respectively. The concentrations of DP increased from the control Station 4_1 to Station 4_3.

In winter 1985 the concentrations of dissolved protein found at the particular stations probably suggest a consequential action of the fertilization. This may confirm the thesis that with a diminished water flow (1.55 dm^3 km^{-2} sec^{-1}) biochemical conversions brought about by a local factor are more precisely illustrated by the state of hydrochemical relations. On this sampling date the content of DP increased down river, at Station 4_3 being almost double that at the control station. This component probably originated from the decomposition of organic matter, previously accumulated on the river bottom as an effect of the mineral fertilization. The occurring processes of breakdown of organic matter were also indicated by other chemical parameters. For example, the concentration of dissolved oxygen decreased from the control station to Station 4_3 with the maximum values of ammonia (B o m b ó w n a unpubl.).

On the other hand, no differences in DOM or DP content were shown by water samples taken during the vegetation season, in July 1983, 1 month after fertilization, with an average constant water flow of 2.5 dm^3 km^{-2} sec^{-1}, and in July 1984 with the an even slower water flow

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(1.88 dm^3 km^{-2} sec^{-1}) and only 9 days after fertilization. The nitrogen from the fertilizers was at that time probably utilized by crop plants and did not penetrate to the river with the ground waters.

6. Polish summary

Wpływ nawożenia azotowego na właściwości chemiczne rzeki Nidy (Polska Południowa) ze szczególnym uwzględnieniem rozpuszczonej materii organicznej

W uzupełnieniu ogólnych badań hydrochemicznych, w okresie od lipca 1983 do maja 1985 roku, badano w rzece Nidzie koncentrację materii organicznej rozpuszczonej (DOM) oraz jej składowej białka rozpuszczonego (DP). Na badanym odcinku rzeki wytypowano 6 stanowisk (ryc. 1).

Woda ze stanowisk 1, 2 w stosunku do wody ze stanowisk zeutrofizowanych 3, 4_1, 4_2, 4_3 była mało zasobna w składniki pokarmowe, takie jak: azotany, azotyny, amoniak i fosforany. Podobnie kształtowały się inne parametry, jak mętność, przewodnictwo i sucha pozostałość (tabela I).

Średnie koncentracje DOM i DP były na poszczególnych stanowiskach mało zróżnicowane (tabela II). Największe ich ilości wystąpiły na st. 2, najmniejsze na st. 1, a pozostałe stanowiska zajmowały miejsce pośrednie. Oba wymienione składniki materii organicznej były skolerowane ze średnimi koncentracjami utlenialności i częściowo ze stratą po prażeniu. Wykazano, że ilości DOM i DP wzrastały w miarę rozwoju wegetacji (od wiosny do lata), a malały w porze jej osłabienia lub zahamowania (od jesieni do zimy).

Ze względu na różne warunki fizjograficzne odcinka wytypowanego pod kątem nawożenia (st. 4_1, 4_2, 4_3) oraz eutrofizację całej dolnej partii rzeki od st. 3 do st. 4_3, wpływ tego zabiegu zaznaczył się bardzo słabo i tylko na wiosnę lub w jesieni. Notowano wtedy sukcesywny wzrost zawartości DP od st. 4_1 do 4_3 (ryc. 2, 3, 4). W próbach wody pobranych dodatkowo w maju 1985 r. z części przybrzeżnej, nawet miesiąc po nawożeniu, przy spadku spływu wody o 1 dm^3 km^{-2} sek^{-1} w relacji do terminu wcześniejszego (ryc. 4) zanotowano wzrastające z biegiem rzeki ilości DP; na st. 4_3 było go nawet o 3,5 mg dm^{-3} więcej niż na stanowisku kontrolnym 4_1. Podobną sytuację w odniesieniu do zawartości DP, świadczącą o następczym działaniu nawożenia zaobserwowano w próbach ze stycznia 1985 roku. Przepływ wody był również minimalny, zaś koncentracje białka wzrastały, a tlenu rozpuszczonego malały z biegiem rzeki. Ponadto notowane maksymalne ilości amoniaku świadczyły o zachodzących procesach redukcji materii organicznej, zdeponowanej wcześniej prawdopodobnie na skutek nawożenia (ryc. 4).

Próby pobrane w połowie lipca w latach 1983 i 1984, a więc w porze zaawansowanej wegetacji, przy niskim i średnim spływie wody, w miesiąc i dziewięć dni po nawożeniu nie wykazywały na poszczególnych stanowiskach zróżnicowanej koncentracji badanych składników. Wskazywałoby to na większe zużycie nawozów przez uprawy w okresie intensywnej wegetacji, przy równocześnie mało widocznym ich wykorzystaniu przez rzeczne organizmy fitoplanktonowe (ryc. 3, 4).

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