POLISH JOURNAL OF ECOLOGY (Pol. J. Ecol.)	50	2	123–135	2002

Regular research paper

Henryk KASZA[1], Joanna GALAS[2]

[1]Technical University of Łódź, Faculty of Textile Engineering and Environmental Protection, Textile Institute, 43-309 Bielsko-Biała, Poland, e-mail: hkasza@pb.bielsko.pl
[2]Karol Starmach Institute of Freshwater Biology, PAS, Sławkowska 17, 31-016 Cracow, Poland, e-mail: galas@zbw.pan.krakow.pl

UPPER VISTULA RIVER: RESPONSE OF AQUATIC COMMUNITES TO POLLUTION AND IMPOUNDMENT. II. CHEMICAL COMPOSITION OF WATER AND SEDIMENT

ABSTRACT: The following paper is a part of the complex studies and intends to provide the background for explaining spatial differentiation of plant and animal communities settled in the Upper Vistula River. The study has been conducted from 10.9 to 336.7 km of the river course. Physico-chemical parameters of water, and nutrient concentrations in surface sediment have been measured. This allowed to discern four zones according to the level of water pollution. The first one, with relatively clean waters, is located in the mountainous part of the Vistula River (to 10.9 km of the river course). The second one – moderately polluted – spreads to 66.2 km. The third zone, with heavily polluted waters, reaches to 248.2 km. The remaining part of the studied river course (to 336.7 km) can be considered as belonging to the fourth zone with considerably polluted waters.

KEY WORDS: Vistula River, water chemistry, sediment, pollution

1. INTRODUCTION

The part of the Vistula River under consideration has been studied many times in respect of its hydrochemical properties. However, former studies concerned much shorter parts of the river. Because of spatially differentiated chemical nature and the state of pollution of the Vistula River these studies can be divided into two groups. The first one contains these concerning relatively clean or comparatively slightly polluted parts of the Vistula River, i.e. starting from the sources to the Goczałkowice Reservoir (Kasza 1986a, 1986b, 1992, Kasza and Winohradnik 1986, Kasza and Krzyżanek 1993, 1995, Dumnicka *et al.* 1988, Wróbel 1995). The second one contains studies on the river between 115.6 km and 336.7 km, i.e. the part of the Vistula River that presently is moderately and strongly polluted (Kotulski 1962, Bombówna and Wróbel 1966, Skoczeń 1981, 1982, Kasza 1988, Schmager 1988, Bombówna 1991, Kamiński and Wróbel 1991, Kownacki 1997).

Irrespective of the above mentioned studies, continuous monitoring of the Vistula River is conducted by the Voivodeship Environment Protection Inspectorates or the Centers of Research and Control of the Environment. The results obtained by these institutions served as the basis for "The Atlas of River Pollution in Poland" (Korol *et al.* 1994).

The amount of organic matter in large, polluted rivers was studied not very often (Leichtfried 1998). The Vistula River sediment has been investigated mainly for the heavy metals content (Pasternak 1974, Pasternak *et al.* 1974, Helios-Rybicka 1983, 1996, Macklin and Klimek 1992), while little attention has been paid to the nutrients level.

The aim of the present work was to study the effects of pollution of the Upper Vistula on selected organisms living in the river. The hydrochemical studies provide the background for explaining the spatial differentiation of plant and animal communities settled in the Vistula River (Bucka 2002, Dumnicka 2002, Kwandrans 2002, Żurek 2002).

2. STUDY AREA

The study has been conducted in the upper Vistula River from 10.9 to 336.7 km of its course. The detailed description of the study area is given by Żurek and Kasza (2002). The samples were collected at nine sampling sites (Figs 1, 2, Table 1).

Sediments (alluvia) of the Vistula River drainage area consist mostly of mud, sand, and gravel (Węcławik 1991) but sand fraction dominates (60–96%), whereas content of clay fraction is much smaller (0.3–11%) (Helios-Rybicka 1986).

3. MATERIALS AND METHODS

The investigation of water chemistry was carried out monthly between March 1996 and March 1997, while sediment samples for carbon, nitrogen, and phosphorus determinations were collected only in June and October 1996 and March 1997.

The water analyses have been performed according to the standard methods (Hermanowicz *et al.* 1976). The concentration of sodium and potassium was determined only once in March 1998. That is why in order to determine the mean ionic content of water, the Na concentration was calculated from the difference of milliequivalents of anions and cations with the concurrent assumption that potassium represents an insignificant percentage of the total content of cations in water of the Vistula River.

Two samples of the surface sediment (sampled to a depth of 5 cm) were randomly taken using a plastic corer (5.5 cm diameter). Sediment samples were transported to the laboratory, air-dried for 48 hours and grounded in a planetary mill. Organic carbon content in dry sediments was measured using chemical oxygen demand (COD) method, total nitrogen was determined by the Kjeldahl method, and total phosphorus by a colorimetric method (APHA 1992).

4. RESULTS

4.1. PHYSICO-CHEMICAL PARAMETERS AND THE ION CONTENT IN WATER

Water temperature in the Vistula River ranged from 1°C up to 22.4°C and was typical for the conditions of this region. The mean annual temperatures of water tended to increase with the course of the river. The pH of water was in the base range (7.2–9.1), excluding the site 1 located in the area exposed to acidified waters of the Czarna Wisełka River (6.6–7.9). The narrower range of pH has been determined in the lower part of the studied Vistula River (Fig. 3).

The water of the Vistula River was characterised by rather high oxygen content ranging between 9–15 mg O_2 l^{-1} in the upper, 4–12 mg O_2 l^{-1} in the middle and 6–12 mg O_2 l^{-1} in the lower course of the studied part of the river (Fig. 3).

The electrolytic conductivity of water fluctuated in a very wide range from 35.7 μS cm^{-1} at the site 1 (10.9 km of the river course) up to the value of 4295 μS cm^{-1} at the site 5 (117.6 km). In the first part of the Vistula River water conductivity oscillated around the value of 100 μS cm^{-1}. On the course of the river from the site 2 (36.6 km) to 4 (66.2 km) the electrolytic conductivity was about 200–350 μS cm^{-1}. From the 89.3 km of the river course (below the mouth of a small river that carries very salty mining waters) to the site 7 (185.2 km) and sometimes up to site 8 (248.2 km) the conductivity of 2000–4000 μS cm^{-1} was most often found. The site 9 (336.7 km) was characterised by conductivity not exceeding 1400 μS cm^{-1} (Fig. 3).

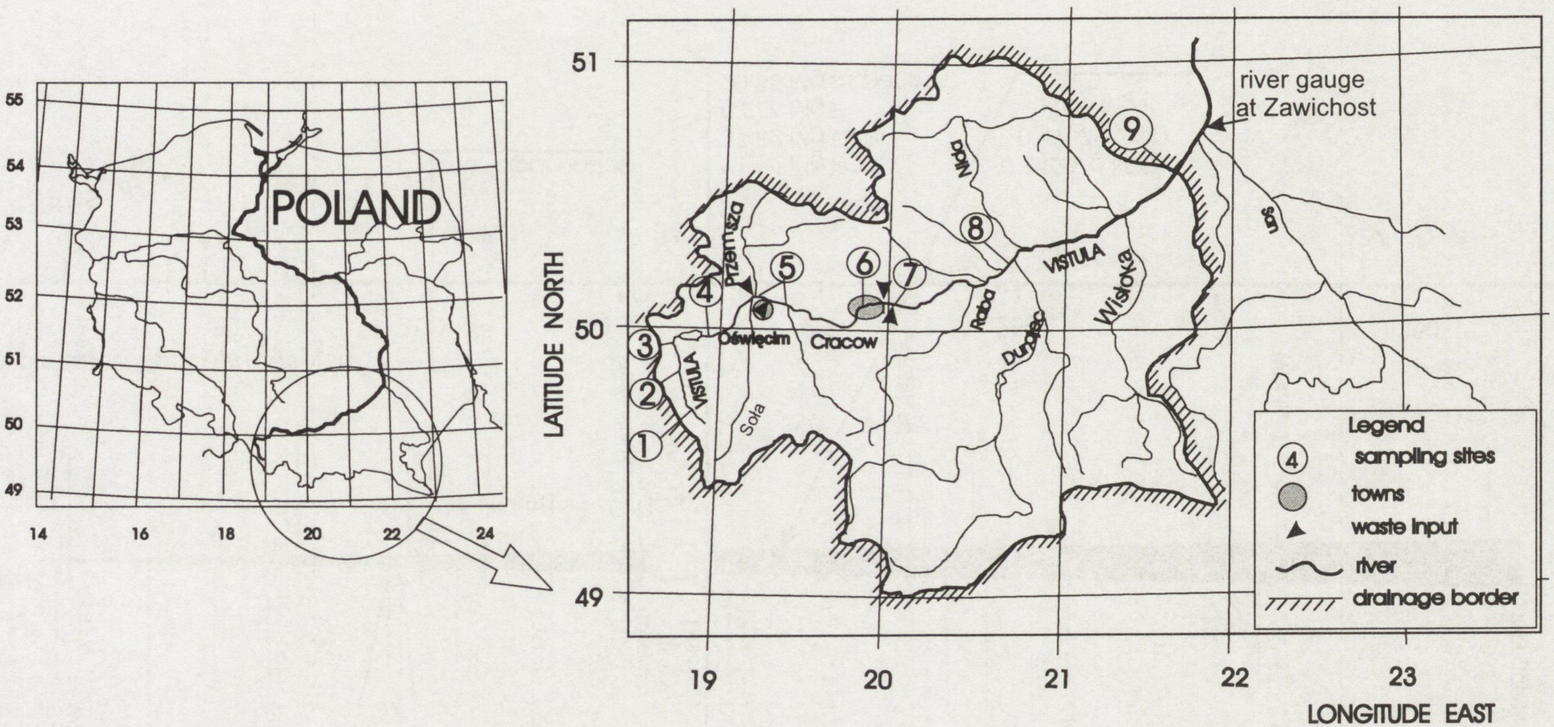

Fig. 1. Map of the study area and the location of the sampling sites (1–9). After Żurek and Kasza (2002).

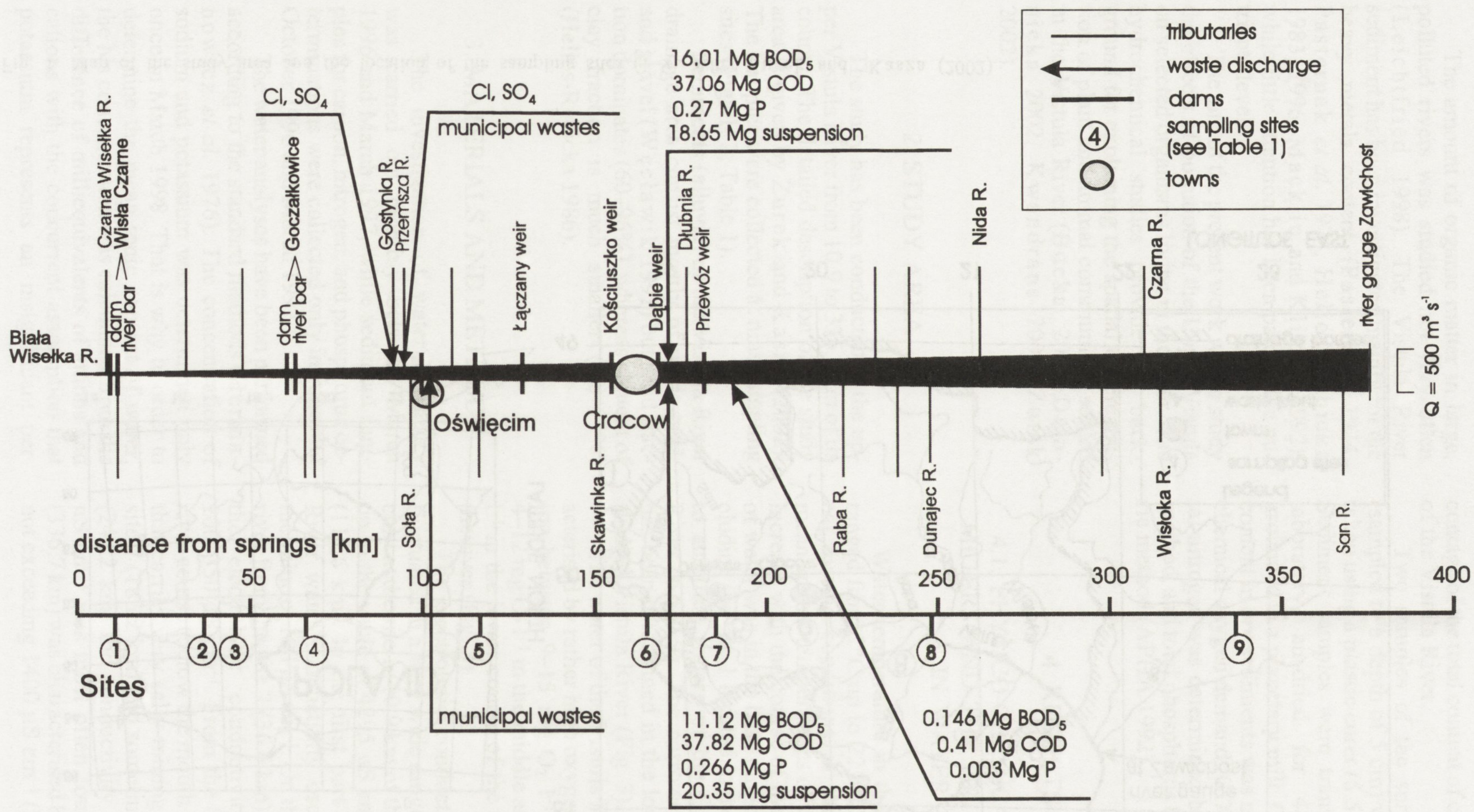

Fig. 2. Scheme of the Upper Vistula River along the increase of the flow. Localisation of sampling sites (1–9), tributaries, dams and towns are given with their respective local names as well as the values of daily load of pollution. After Żurek and Kasza (2002).

Table 1. Localisation and characteristics of sampling sites

Stations	Distance (km)	Beds and deposits	Remarks
Site 1 (Wisła Czarne)	10.9	stones	mountainous part of the river, slight loading of sewage
Site 2 (Skoczów town)	36.6	gravel, pebble, cobble and coarse sand	effluents from sewage treatment plants (small towns)
Site 3 (Drogomyśl village)	45.7	gravel, pebble, coarse sand	effluents from ponds and purification plant at Skoczów town
Site 4 (Goczałkowice Zdrój)	66.2	coarse sand and sandy clay	outflow from Goczałkowice dam reservoir
Site 5 (Jankowice village)	117.6	sand	mining waters providing by Gostynia and Przemsza tributaries, rich in Cl^-, SO_4^{-2}, NO_3^-, PO_4^{-3}, suspension as well as municipal and industrial wastes from Silesia region and Oświęcim town
Site 6 (Cracow)	167.8	sand in the channel, mud at the banks	influence of Cracow town, Cl^-, SO_4^{-2}, suspension, organic matter
Site 7 (Przylasek Rusiecki village)	185.2	sand, locally mud	site 2 km below the outflows of municipal wastes from Cracow
Site 8 (Opatowiec)	248.2	mud, clay between meander spur, sand in channel	25 km below inflow of clear water of large Raba river
Site 9 (Machów village)	336.7	sand in channel, mud at the banks, sandy islands	90 km below inflow of clear water from Dunajec river

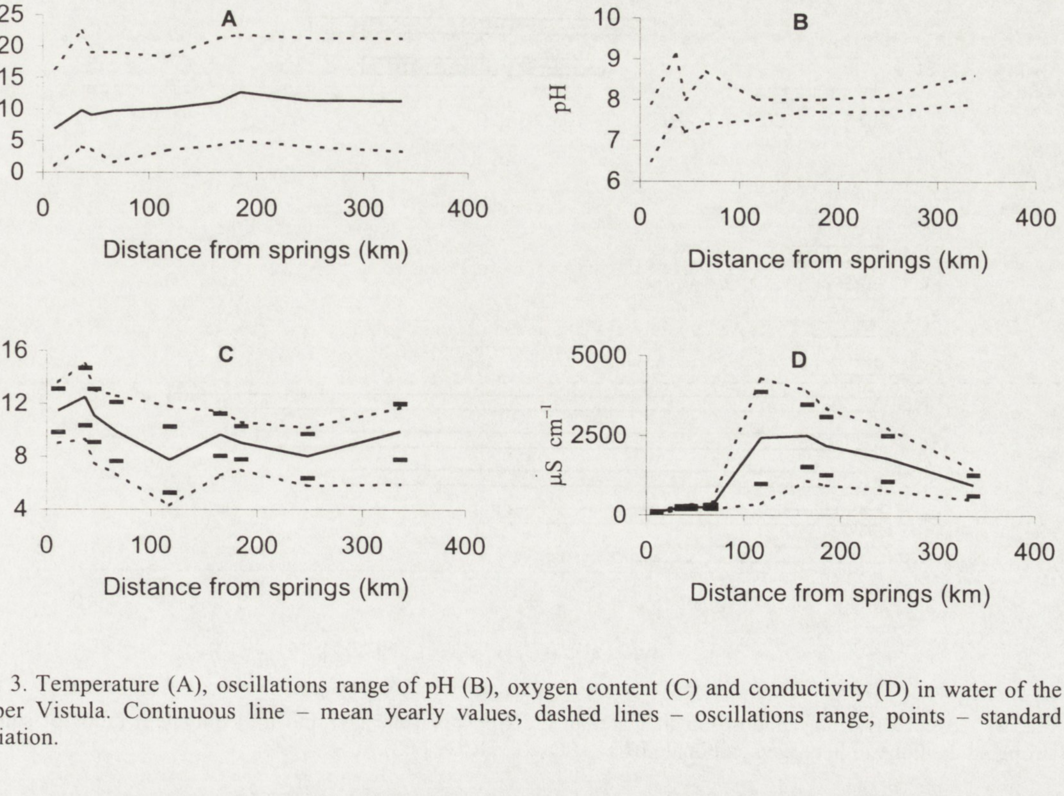

Fig. 3. Temperature (A), oscillations range of pH (B), oxygen content (C) and conductivity (D) in water of the Upper Vistula. Continuous line – mean yearly values, dashed lines – oscillations range, points – standard deviation.

The main factor causing this huge differentiation of the electrolytic conductivity were the chlorides, and among them sodium chloride (Fig. 4). The mountainous part of the Vistula River (station 1) was characterised by low concentrations of chlorides about 2–5 mg Cl l^{-1}. In the remaining course of the Vistula River concentrations of chlorides were: from the site 2 to 4: 10–20 mg Cl l^{-1}, from the site 5 to 8: 500–1300 mg Cl l^{-1}, below the site 8: 100–300 mg Cl l^{-1}. At the site 5 there was a shift of water type from that characteristic to the majority of surface waters bicarbonate – calcareous to chloride – sodic. The amount of strong acid anions increased as well, i.e. chloride and sulphate anions to cost of decreasing amount of carbonates. During the course of the river gradual improvement in the mutual ratios of these anions has been observed to the advantage of carbonates (Fig. 4).

4.2. NUTRIENTS IN WATER

The concentrations of mineral forms of nitrogen (nitrate and ammonia) and their relative proportions in the total concentration of this nutrient in water of the Vistula River (Fig. 5) depended on pollution sources and loads of wastewaters. In the mountainous part of the Vistula, where the river was exposed to slight loading of sewage, the sum contents of ammonia and nitrate nitrogen was small (1 mg N l^{-1}). The ammonia nitrogen constituted about 1/3 of all mineral nitrogen. Below small towns the contents of mineral nitrogen increased slightly above 2 mg N l^{-1} (site 2). The increase was caused by nitrates. At the site 5, because of pollution inflow from the Silesia region and Oświęcim town (Fig. 2), the amount of mineral nitrogen increased to 3 mg N l^{-1}. The ammonia nitrogen was respon-

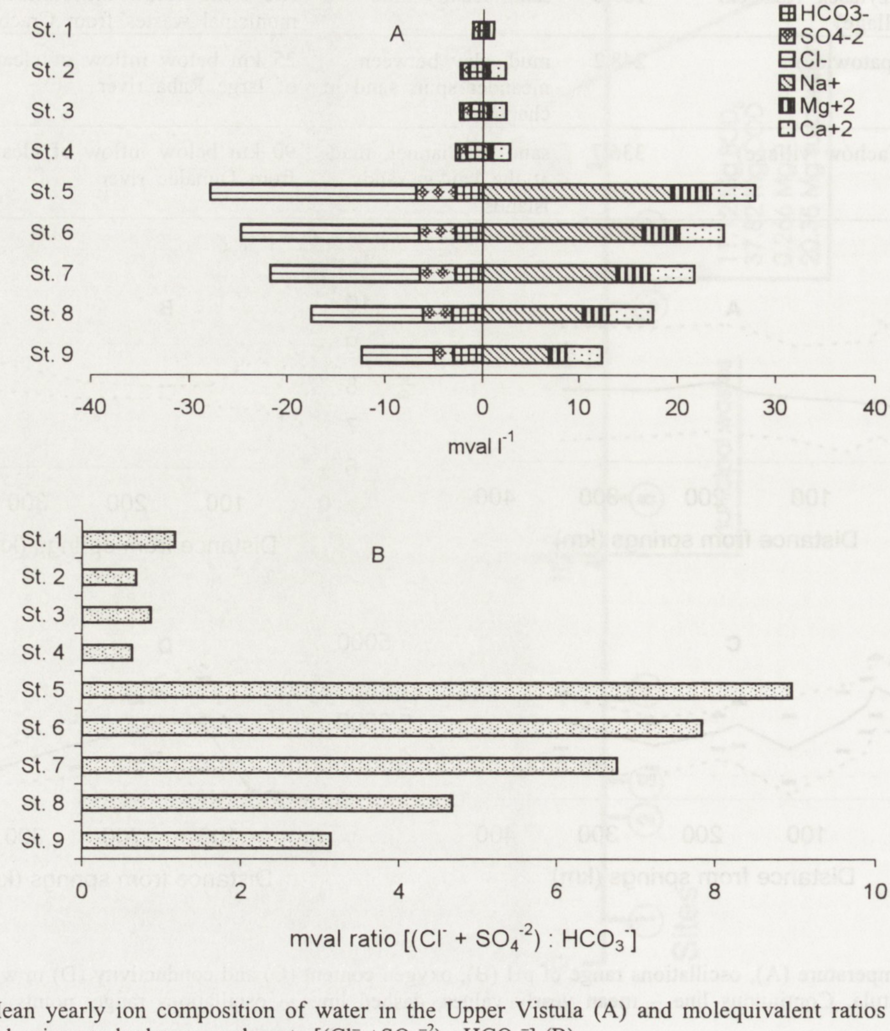

Fig. 4. Mean yearly ion composition of water in the Upper Vistula (A) and molequivalent ratios of sum of strong acid anions to hydrogen carbonate [(Cl^- +SO_4^{-2}) : HCO_3^-] (B).

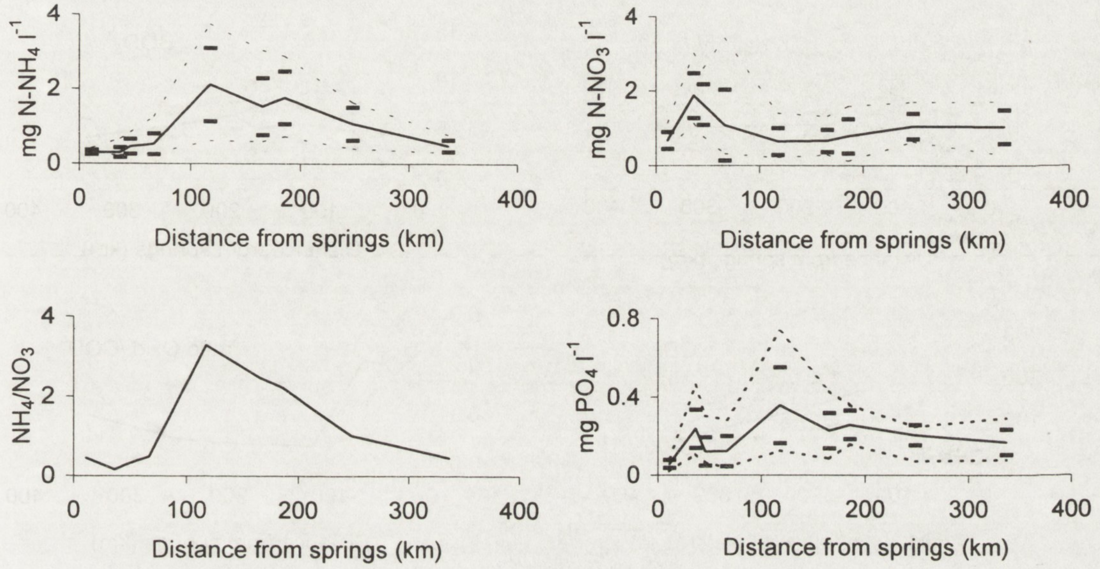

Fig. 5. Content of ammonia nitrogen, nitrate nitrogen, phosphates and ratio of NH_4 : NO_3 in water of the Upper Vistula (continuous line – mean yearly values, dashed line – oscillations range, points – standard deviation).

sible for that rise, since it represented 80% of mineral nitrogen. The more distinct decrease in nitrogen concentration has not been noticed till the site 8 (248.2 km). Together with the decrease in its concentration the gradual change of ratios of mineral forms of this nutrient has taken place, i.e. nitrate nitrogen increased and ammonia nitrogen decreased.

The changes in phosphates concentrations (Fig. 5) occurred in a similar manner as those of mineral nitrogen compounds. The increase in concentrations of that component took place below the discharge of wastewaters from small towns (site 2). Along with the course of the river the amount of phosphates decreased. The following abrupt increase in phosphates was noted after the inflow of wastewaters from the Silesia region and Oświęcim town (Fig. 2). In the following course of the river the content of phosphates decreased.

4.3. POLLUTION OF THE VISTULA RIVER WITH ORGANIC COMPOUNDS

On the basis of BOD_5 the Upper Vistula River could be divided into two different parts. In the first part biological oxygen demand was in most cases lower than 4 mg O_2 l^{-1} (Fig. 6). Such values of BOD_5 were recorded in the upper course of the Vistula River till the Goczałkowice Reservoir (61.2 km). The second part of the river, where the water was characterised by BOD_5 values higher than 4 mg O_2 l^{-1}, spreads from the site 4 to 9, but starting from the site 7 the gradual decrease of BOD_5 could be noticed.

The content of organic compounds in water of the Vistula River as determined by oxidability was similar to that assessed with BOD_5. Relatively low values of oxidability have been recorded in water of the Vistula River from the upper course till Goczałkowice Reservoir (Fig. 6). Considerably higher values of oxidability have been found below the reservoir and distinctly higher in the Vistula below.

The values of COD were relatively low in the part from the site 1 to 4. Starting from the site 5 chemical oxygen demand in the Vistula River water increased 10-fold and remained relatively high along the further course of the river, however, gradually decreasing (Fig. 6).

The ratio of oxydability to COD showed that in the upper course of the Vistula River (till the inflow of industrial pollutions from Silesia region and Oświęcim town) readily biodegradable compounds represented about 20% of the total content of organic compounds. Below the site 5 the contribution of organic substances readily oxygenated by po-

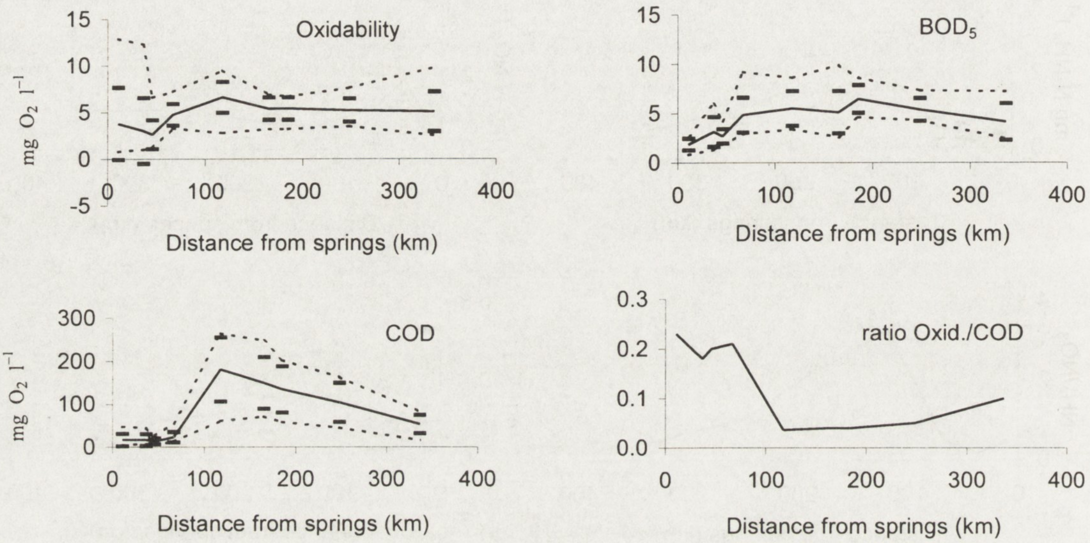

Fig. 6. Oxidability, BOD_5, values of COD and ratio of oxidability to COD in water of the Upper Vistula. Continuous line – mean yearly values, dashed lines – oscillations range, points – standard deviation.

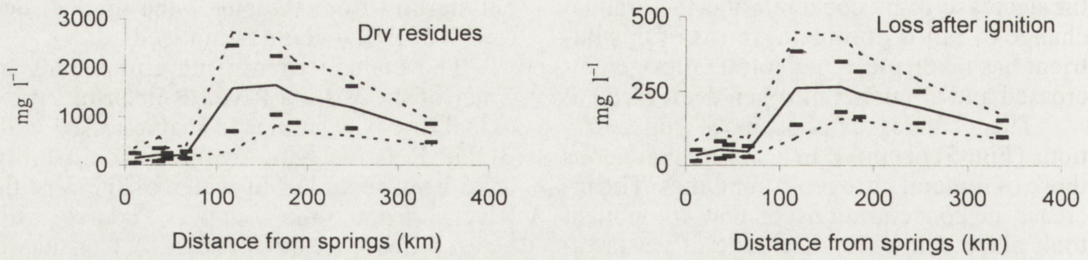

Fig. 7. Dry residues and loss after ignition in water of the Upper Vistula. Continuous line – mean yearly values, dashed lines – oscillations range, points – standard deviation.

tassium permanganate in the total content of these compounds was even lower, that is barely 4%. However, starting from this sampling site some improvement in these relations could have been noticed.

The loss after ignition as an additional approximate indicator of water pollution with organic matter confirmed the high content of organic compounds in the Vistula River, starting from the site 5 (Fig. 7).

4.4. SEDIMENT

The pattern of changes of organic carbon, nitrogen, C/N ratio and total phosphorus concentrations in the river sediment is shown in Fig. 8. The highest concentration of the organic carbon (40 mg C g^{-1}) was found at the site 5. Down with the river course it decreased to the value of 9 mg C g^{-1} (the site 6 and 7). A small increase was also stated in the site 8 and 9. Distribution of total nitrogen re-

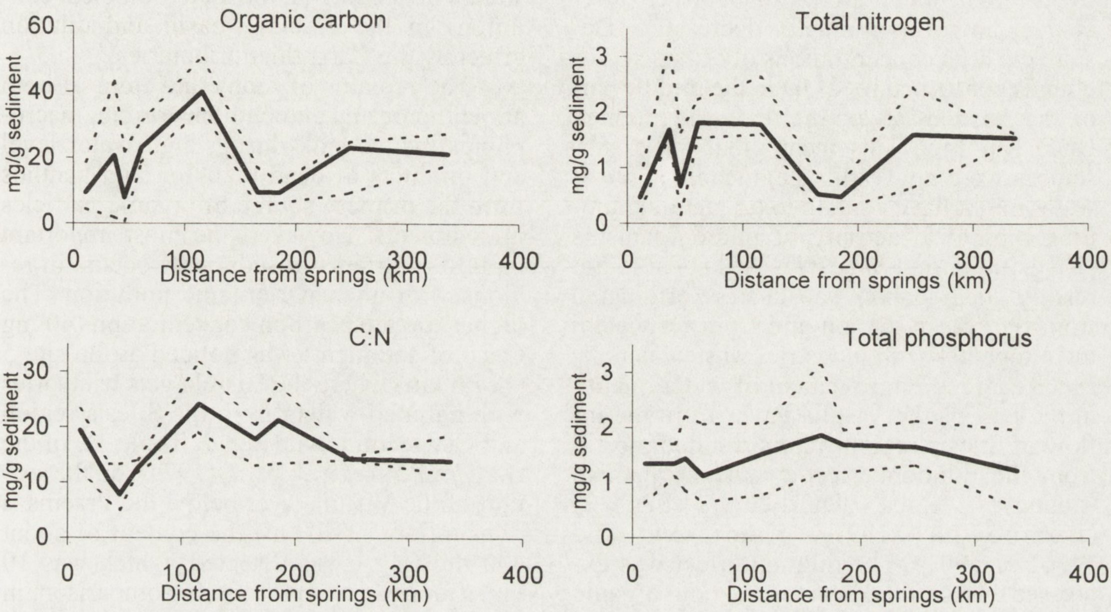

Fig. 8. Nutrient content in sediments of the Upper Vistula: organic carbon, total nitrogen, C:N ratio and total phosphorus content. Continuous line – mean yearly values, dashed line – oscillations range.

sembled that of organic carbon. The highest value of this nutrient were detected at the site 2 and 5: 1.68 and 1.81 mg N g^{-1}, respectively. The second maximum was noted at the site 8 (1.60 mg N g^{-1}). The smallest values were found at the site 1, 6 and 7 (around 0.5 mg N g^{-1}). The down stream (from the site 1 to 3) decrease in the C:N ratio followed by its increase up to the maximum values at the sites 5 and 7 was found. The concentration of total phosphorus was 1.34 mg P g^{-1} at the station 1, then it decreased to the value of 0.6 mg P g^{-1} at the site 4. The second increase was observed at the site 6 (1.87 mg P g^{-1}), and the next decrease was noted at the site 9 (1.23 mg P g^{-1}).

5. DISCUSSION

The Vistula River in its upper part was medium mineralised river with bicarbonate – calcareous type of water. After the inflow of one small tributary (89.3 km of the Vistula course) and Przemsza river (93.1 km of the Vistula course) the type of water changed into chloride-sodic and remained such along the studied distance of the river with the content of electrolytes gradually decreasing. The increase in electrolyte content was caused by loading of mining waters from the Silesia region and their long-range action on the degree of mineralization and salting of waters of the Vistula. The inflow of industrial and municipal wastes from Oświęcim and Cracow town additionally increased the pool of macroelements in waters of the Vistula (Kamiński and Wróbel 1991).

The content of nutrient compounds in the Vistula River was high and according to the criteria given by Vollenweider (1968) this can stimulate the development of phytoplankton in an aquatic environment. With the course of the river the Vistula was enriched by nutrients loaded by polluted inflows. After the inflow of wastewaters from the Silesia region and municipal and industrial wastes from Cracow the ammonia nitrogen dominated over nitrate nitrogen, what is characteristic for heavily polluted rivers. Besides the inflow of ammonia nitrogen together with municipal and industrial wastewaters the inhibition of nitrification caused such an arrangement of mineral forms of nitrogen in this heavily polluted river (Kamiński and Wróbel 1991).

Starting from the site 5 chemical oxygen demand in water of the Vistula River increased almost 10-folds and remained at relatively high level along the further river course, however gradually decreasing. Despite the high concentrations of organic compounds confirmed by COD in the middle part of the Vistula River, the above mentioned BOD was low. This means that these substances were not readily degradable and that water might have contain toxic factors inhibiting biological activity of microorganisms (Kamiński and Wróbel 1991). These not readily degradable substances originated from the Silesia region and from Oświęcim town together with industrial wastewaters.

Recorded improvement of water quality in the part of the Vistula River from the inflow of Silesia region waters resulted mostly from the dilution effect by the Carpathian tributaries (Raba, Dunajec – Fig. 2) (Bombówna 1991, Kamiński and Wróbel 1991). The dilution effect was expressed as a gradual decrease of both organic compounds and nutrients concentration along the river course. This was also the cause for the decrease in the degree of mineralisation.

Taking into account the chemical content and the degree of water pollution in the Upper Vistula four zones could be distinguished. The first one with relatively clean waters is located in the mountainous part of the Vistula River. The second one – moderately polluted – spreads to the site 4, or possibly somewhat further to the mouths of rivers carrying municipal and industrial wastewaters from the Silesia region. The third zone with heavily polluted waters reaches the site 8. The remaining part of the studied river section can be considered as the fourth zone with considerably polluted waters (Table 2). The range of the above mentioned zones is not stable and may move upstream or downstream depending on the meteorological conditions in the drainage basin and dilution effect by the Carpathian tributaries.

The remains of fauna and flora of both allochthonic and autochthonic origin, macrophytes, which sink during high water level and products of dead plankton and benthos form the primary source of organic particles in sediments. However, the most important input of nutrients in sediments occurs in regions with intensive organic pollution. The highest organic carbon concentration (40 mg C g^{-1} of sediment) was noticed at the site 5 (117.6 km) where the Vistula gets tributaries with polluted waters from the Silesia region and Oświęcim town (Fig. 2, Table 1). In the study of Pasternak *et al.* (1974), on the section of the Vistula river below the Przemsza river inflow (93.1 km) the content of about 400 mg C g^{-1} was detected, which was 10 times more than at present. In comparison, in the Elbe river, one of Europe's most contaminated large rivers, in its not-tidal section with anthropogenic and industrial sources of pollution, organic carbon content was 130 mg C g^{-1} (Brügmann 1995).

At the sites 6 and 7 (below the steal factory in Cracow) the amount of organic matter in sediments decreased significantly to the value of 7 mg C g^{-1}. That fall resulted from the presence of weirs and sluices situated above these stations and from settling down of suspension carried in water. Also intensive processes of river self purification and high share of relatively clean waters of the affluents in the total mass of the river may cause the decrease in this nutrient level. Similar reduction of organic carbon content in the Vistula River sediments between 167 and 307 km of the river course was noted at the beginning of 70-ties (Pasternak *et al.* 1974).

Table 2. Pollution zones of water in the Upper Vistula (from springs to 336.7 km of the river course) and their hydrochemical characteristics (min – max., data from March 1997 to March 1998)

Zone	Extent of zone	Conductivity ($\mu S\ cm^{-1}$)	$N\text{–}NO_3$ (mg l^{-1})	$N\text{–}NH_4$	PO_4	COD
With relatively clean water	mountain section<10.9 km	35–120	0.4–1.1	0.2–0.4	0.02–0.08	5–50
Moderately polluted	10.9–66.2 km	160–350	0.3–3.4	0.2–1.2	0.04–0.46	5–55
Heavily polluted	66.2–248.2 km	350–4300	0.1–1.6	0.6–3.0	0.09–0.75	60–265
Considerably polluted	248.2 km–336.7[1]	490–1400	0.3–1.7	0.3–1.6	0.07–0.30	15–160

[1])The range of the zones may move upstream or downstream depending on meteorological conditions in drainage basin and dilution effect by Carpathian tributaries.

The C:N ratio provides a measure of the organic matter composition (age, source) in sediments (Walling *et al.* 1997). Its maximum value (30) in this study was noted at the site 5, which may reflect the presence of organic contamination in this area (Table 1). The C:N ratio in sediments of very contaminated rivers ranges between 27–47 (Pasternak *et al.* 1974).

The amount of nutrients in sediment is associated with its grain size composition; elevated level of organic nitrogen and carbon is found with fine sediments (Johnston *et al.* 1984) while in coarse sediments the concentration of these nutrients is lower. At two sites: 1 and 3 where bottom consists of stones and gravel (Table 1), low concentrations of organic carbon follow that rule. Along the river course the changing nature of the bottom with more fine sediments caused the increase in nutrient content at the sites 5, 8 and 9. Sediments at the site 6 and 7 comprise mostly sandy material, so their organic carbon and total nitrogen levels are low.

The average concentration of phosphorus in the studied sediments ranged from 1.1 to 1.9 mg P g^{-1}, of generally industrial and agricultural origin. Especially notable share in the elevated concentration of sediment phosphorus at the Cracow site may be form communal sewer outflow since significantly higher concentrations of this nutrient are reported in the urbanised areas (Huanxin *et al.*1997). The intensive dredging works, which were carried in the autumn of 1997 at this river section may also have some effects on increased phosphorus level in the sediment.

River alluvia containing small organic particles usually serve as a substrate and food for the smallest benthic invertebrates e.g. Oligochaeta communities. Investigations of their quantity using also the corer method were carried out at the same time, in the Vistula River between sites 5 and 9 (Dumnicka 2002). The positive correlation between the density of Oligochaeta and nutrient contents which was found in this river section in March 1998 may reflect the availability of organic matter for this fauna within the substrate. Similar dependence between organic matter and Oligochaeta number was found in mountain stream sediments (Dumnicka and Galas 1997).

6. SUMMARY

The aim of this study was to assess the effects of pollution of the Upper Vistula on selected organisms living in the river. The hydrochemical studies provide the background for explaining the spatial differentiation of plant and animal communities settled in the Vistula River. The investigations of water chemistry were carried out monthly between March 1996 and March 1997, while surface sediment samples for carbon, nitrogen and phosphorus determinations were collected only in June and October 1996 and March 1997. The studies were conducted between 10.9 and 336.7 km of the Vistula course, at 9 sampling sites (Figs 1, 2, Table 1).

Physical and chemical parameters of water, the ion content (Fig. 3, 4), nutrient concentrations (Fig. 5) and pollution with organic carbon (Figs 6, 7) were measured. Nutrient concentrations in sediment were also analysed (Fig. 8).

Taking into account the chemical content and the degree of water pollution in the Upper Vistula four zones could be discerned. The first one with relatively clean waters is located in the mountainous part of the Vistula River (to 10.9 km of the river course). The second one – moderately polluted – spreads to 66.2 km of the river course (probably up to the mouths of polluted rivers carrying municipal and industrial wastewater from Silesia region). The third zone with heavily polluted waters spreads to 248.2 km. The remaining part of the studied river section can be considered as the fourth zone with considerably polluted waters (Table 2). The range of the above mentioned zones is not stable and may move upstream or downstream depending on the meteorological conditions in the drainage basin and dilution effect by the Carpathian tributaries.

Concentrations of total carbon and nitrogen in sediment were the highest in areas close to industrial pollution sources, while the highest phosphorus content was found near urban agglomerations (Fig. 8).

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(*Received after revising July 2001*)