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Concentrations and loads of N-NO_3, N-NH_4, PO_4 and BOD_5 in waters of the upper Dunajec (in the years 1985–1998)

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Abstract: Loads of N-NO_3, N-NH_4, PO_4 and BOD_5 carried in surface waters of the upper Dunajec catchment basin (at the section in Krościenko) in the years 1985–1998 are presented in this paper. Water quality of the Biały Dunajec (in Szaflary), Czarny Dunajec (in Ludźmierz) and Dunajec (in Krościenko) was characterised. Annual loads discharged from the area per km^2 of the catchment were calculated from mean annual flows (*SQ*) and concentrations of studied components in river waters. Concentration of N-NO_3 in waters of the Biały Dunajec was more than two times higher and that of phosphates – over seven times higher than the respective concentrations in the Czarny Dunajec and Dunajec. Different population density, numerous tourists and low level of water and sewage infrastructure were responsible for these differences.

Key words: *loads of N-NO_3, N-NH_4, PO_4, SSQ flows, surface waters*

INTRODUCTION

Mountain conditions favour the transport of chemical substances to surface waters. Nutrients which enhance the blooms of phytoplanktonic algae pose the greatest threat to the quality of streams and rivers (MAZURKIEWICZ-BOROŃ, 2002).

Basic source of nitrogen discharge to waters is the surface runoff, phosphorus originates mainly from point sources (PAWLIK-DOBROWOLSKI, 1990). Particularly noxious are crude (untreated) waste waters delivered directly to surface waters. They contain various harmful mineral and organic substances (MACIAK, 1999).

Domestic and agricultural sources are the main pollutants present in the upper Dunajec catchment basin. They affect the status of surface waters and the load of components discharged in waters flowing out of the area. Recent years have brought positive changes in Podhale as in the whole country (KOZŁOWSKI, 2001) like e.g. the decline of mineral fertilisers or herbicide doses, more efficient use of natural fertilisers and gradual improvement of water management and sewage handling within rural settlements. Increased pollution of some waters by ammonium and phosphate ions should be considered a negative phenomenon (RACZAK, 2002).

The aim of presented study was to determine concentrations and loads of $N\text{-}NO_3$, $N\text{-}NH_4$, PO_4 and BOD_5 in waters of the upper Dunajec measured in Krościenko in the years 1985–1998. The problem is important in view of intensive development of tourism which is suspected of generating pollution and decreasing surface water quality.

STUDY AREA

The Dunajec is the main river draining Podhale. It was formed by joining the Biały and Czarny Dunajec in Nowy Targ. Studied part of the upper Dunajec catchment (to the section in Krościenko) covers an area of 1580 km^2. Partial catchments of the Biały Dunajec (down to Szaflary) and Czarny Dunajec (down to Nowy Targ) occupy 210 and 432 km^2, respectively (Atlas..., 1995–1996).

Annual sums of atmospheric precipitation are high ranging from 800 mm (Nowy Targ – Orawa Valley) to 1800–2000 mm in topmost parts of the Tatra Mountains (Atlas..., 1985; NIEDŹWIEDŹ and OBRĘBSKA-STARKLOWA, 1991). Such precipitation results in substantial discharge whose long term mean values in the catchment of the Czarny Dunajec (section Nowy Targ) amounted 285 million $m^3 \cdot y^{-1}$ (at mean annual *SSQ* flow – 9.03 $m^3 \cdot s^{-1}$). For the Biały Dunajec (in Szaflary) and for the whole upper Dunajec in Krościenko the respective figures are 167 million $m^3 \cdot y^{-1}$ and 970 million $m^3 \cdot y^{-1}$ (at SSQ = 5.32 $m^3 \cdot y^{-1}$ and 30.8 $m^3 \cdot y^{-1}$, respectively) (Atlas..., 1995–1996; ŁANIEWSKI, 1997).

Long term mean annual temperature in moderately cool storey of studied area ranges between 6 and 4°C, in the uppermost parts (the Tatra Mts – cold storey) this temperature was –1 to –2°C.

Population density in the upper Dunajec catchment basin was relatively high and averaged 160 ind.$\cdot km^{-2}$ and in the catchment of Biały Dunajec it was even higher – 192 ind.$\cdot km^{-2}$. Additionally, many people stay there for vacations and recreation. During the tourist season their number may reach as many as 40% of permanent inhabitants (SMOROŃ and TWARDY, 2004). Tourist services in the catchment basin of the Czarny Dunajec are carried out to a limited extent and only in its south-eastern part in the commune Kościelisko (SMOROŃ and TWARDY, 2003). Population density was low there and averaged c. 60 person$\cdot km^{-2}$ (Rocznik..., 1986; 1989; 1993; 1997; www.stat.gov.pl). In 1998 sewage treatment plants in the Biały Dunajec catchment basin received sewage from 45.5% population and in the Czarny Dunajec catchment – from only 4.8% (www.stat.gov.pl). In the studied Dunajec catchment basin to the section in Krościenko c. 42% inhabitants channeled their sewage to sewage treatment plants.

In the study period remarkable changes occurred in land use structure and farm animal stock within administrative units of the upper Dunajec catchments. Contribution of arable lands to total farmlands decreased by c. 38% in favour of meadows and pastures (from 40.0 to 78.0%). Percentage of forests in total area increased from 35.6 to 39.3%. These changes were still more distinct in the catchment basin of the Biały Dunajec. The area occupied by arable lands decreased to only 9% of croplands and the contribution of meadows and pastures exceeded 90%. Forested area increased from 43.7 to 48.6%.

Decline in the stock of farm animals was also observed in the study period. It was greatest in the catchment basin of the Czarny Dunajec (from 107.5 LU/100 ha in 1985 to 77.3 LU/100 ha in 1996). Less decline of animal stock (by 27.2 LU/100 ha i.e. from 107.8 to 80.1 LU/100 ha) was observed in the Biały Dunajec catchment and in the whole catchment basin of the upper Dunajec (by 25.1 LU/100 ha i.e. from 98.5 to 73.4 LU/100 ha).

METHODS

Changes in water pollution of the Biały and Czarny Dunajec and in the Dunajec at Krościenko in the years 1985, 1990, 1992, 1996 and 1998 were analysed based on annual concentrations calculated from monthly analyses of water samples. The results of water analyses (N-NO$_3$, N-NH$_4$, PO$_4$ and BOD$_5$) were obtained from WIOŚ in Nowy Sącz for sampling sites in Szaflary (Biały Dunajec – point I),

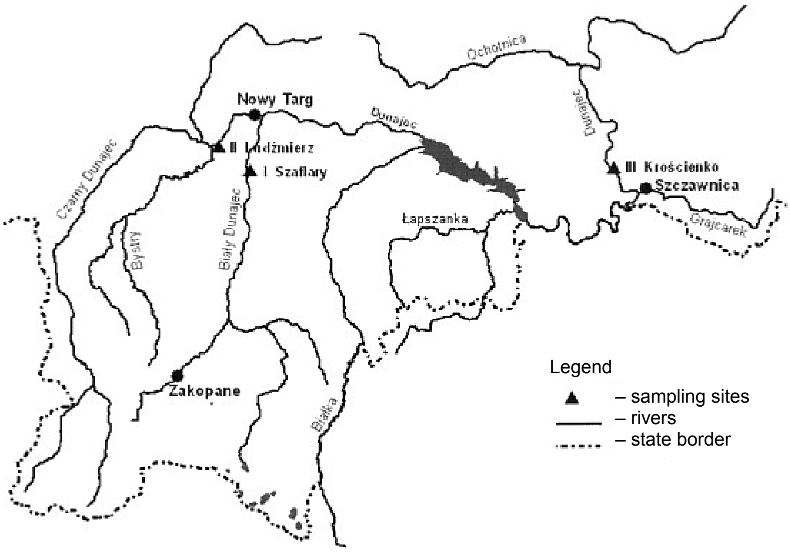

Fig. 1. Location of sampling sites of water for chemical analyses

Ludźmierz (Czarny Dunajec – point II) and Krościenko (Dunajec – point III). The sampling sites are shown in Fig. 1. Analyses were performed with methods used in the State Environmental Monitoring. Mean annual water flows in sampling sites obtained from IMGW, Kraków Branch were used to calculate loads. Annual loads of chemical components were presented per km^2 of particular catchments.

RESULTS

Annual water discharges during the period under study in the Biały and Czarny Dunajec were slightly lower from long term (1951–1990) data and amounted 5.21 and 8.99 $m^3 \cdot s^{-1}$ or 24.8 and 20.8 $dm^3 \cdot s^{-1} \cdot km^{-2}$, respectively. The mean annual discharge in the Dunajec was higher – 33.26 $m^3 \cdot s^{-1}$ (i.e. 21.1 $dm^3 \cdot s^{-1} \cdot km^{-2}$). The highest mean annual flows in studied rivers were noted in 1985, the lowest – in 1990 except for the Czarny Dunajec, where the lowest discharge occurred in 1992 (Fig. 2).

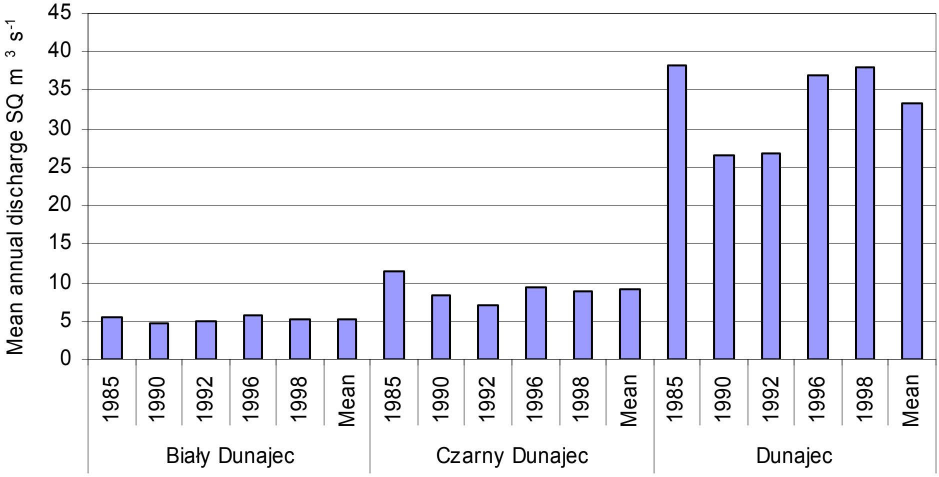

Fig. 2. Mean annual flows (*SQ*) in the Biały Dunajec, Czarny Dunajec and Dunajec in the years 1985–1998

Concentrations of some chemical components in studied rivers varied considerably. This was particularly true for PO_4 whose mean concentration in the Biały Dunajec (0.31 $mg \cdot dm^{-3}$ was 4–8 times that in the waters of other rivers (Fig. 3). The highest concentration of phosphates in waters of the Biały Dunajec was noted in 1996 (0.40 $mg \cdot dm^{-3}$), the lowest – in 1985 (0.19 $mg \cdot dm^{-3}$). In waters of the Czarny Dunajec the variability of phosphate concentrations around the mean from

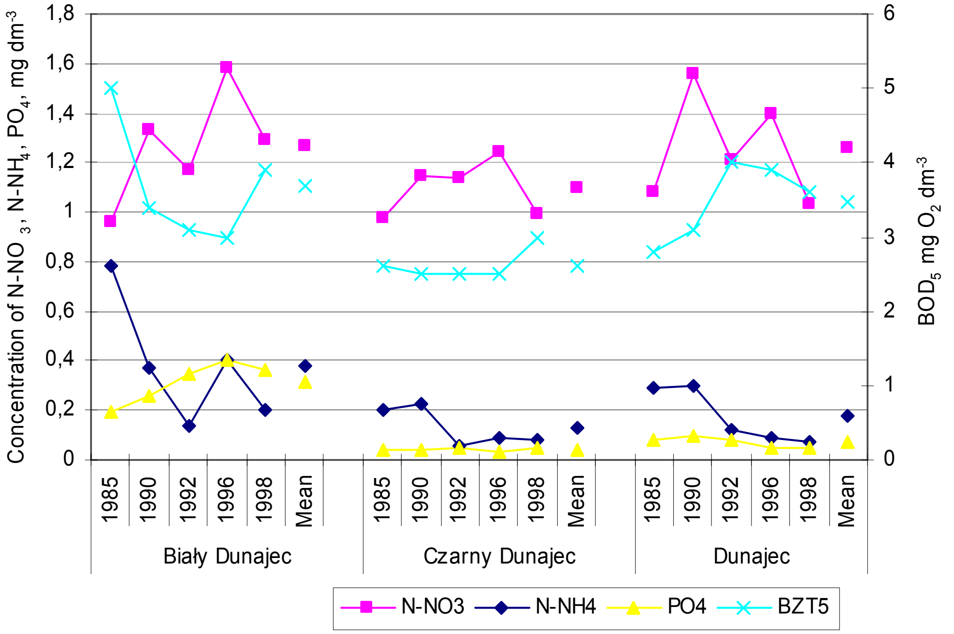

Fig. 3. Mean annual concentrations of N-NO$_3$, N-NH$_4$, PO$_4$ and BOD$_5$ for the years 1985–1998 and the means for the whole study period in waters of the Biały Dunajec, Czarny Dunajec and Dunajec

the study period (0.04 mg·dm^{-3}) was much smaller and amounted 0.01 mg dm^{-3}. Mean concentration of phosphates in the Dunajec was 0.07 mg PO_4 dm^{-3} and their lowest concentration (0.04 mg·dm^{-3}) was noted in the years 1996–1998.

Concentration of ammonium ions were less differentiated in waters of the studied rivers. Mean (1985–1998) annual concentration of ammonium nitrogen in the Biały Dunajec was 0.38 mg·dm^{-3} being 2–3 times higher than in other rivers. The highest concentrations of N-NH$_4$ in waters of the Biały Dunajec and Dunajec were noted in 1985 (0.78 and 0.29 mg dm^{-3}, respectively) and those in the Czarny Dunajec – in 1990 (0.23 mg dm^{-3}, Fig. 3).

Mean concentrations of nitrate nitrogen were similar in the Biały Dunajec and Dunajec (1.26–1.27 mg dm^{-3}) and slightly lower (1.10 mg dm^{-3}) in the Czarny Dunajec. Nitrate concentrations in the Biały Dunajec tended to increase with time and in the Dunajec – to decrease slightly. Only in waters of the Czarny Dunajec nitrate concentrations were similar in particular study years and their variation around the mean of the years 1985–1998 did not exceed 0.14 mg N-NO$_3$ dm^{-3}.

Mean concentrations of BOD$_5$ in waters of the Dunajec and Biały Dunajec were 3.48 and 3.68 mg O_2 dm^{-3}, respectively, being higher than the mean for the Czarny Dunajec (2.62 mg O_2 dm^{-3}). There was a decreasing tendency of these concentrations in the Biały Dunajec (from 5.00 in 1985 to 3.00 mg O_2 dm^{-3} in 1996) but in waters of the Dunajec BOD_5 increased from 2.80 to 3.60 mg $O_2 \cdot dm^{-3}$. In the Czarny Dunajec BOD_5 remained constant at a level of 2.55 mg $O_2 \cdot dm^{-3}$ to the year 1996 and in the last year of study it increased to 3.00 mg $O_2 \cdot dm^{-3}$ (Fig. 3).

Waters discharged from the Biały Dunajec catchment basin carried the highest unit loads of analysed components. Mean annual load of nitrates was 992.3 $kg \cdot km^{-2} \cdot y^{-1}$ (Fig. 4). The highest load of nitrates was noted in 1996 (1359.6 $kg \cdot km^{-2} \cdot y^{-1}$), and the lowest in 1985 (804.4 $kg \cdot km^{-2} \cdot y^{-1}$). Loads increased with time during the study period.

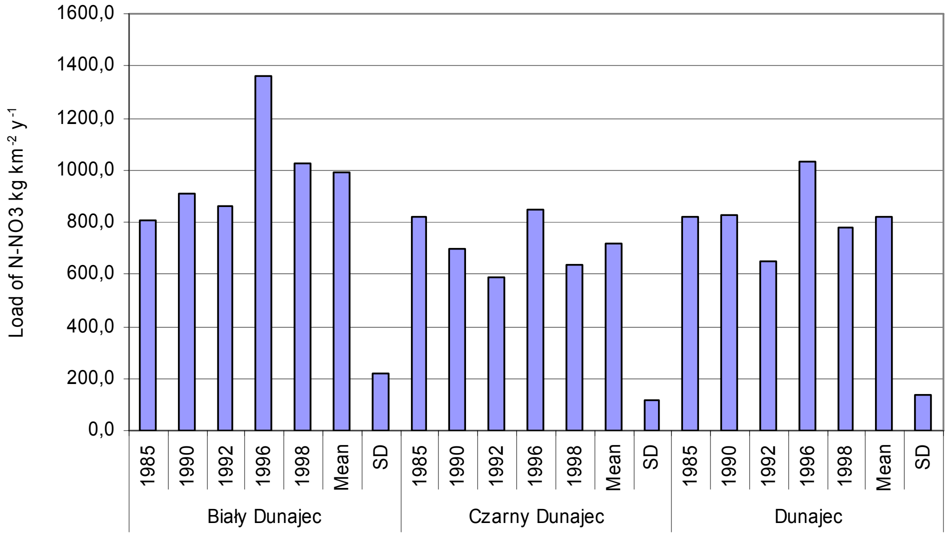

Fig. 4. The loads of $N\text{-}NO_3$ discharged in particular years of the period 1985–1998 and mean values and standard deviations for the whole period

The load of nitrates in waters of the Czarny Dunajec was smaller by c. 28% and averaged 717.1 $kg \cdot km^{-2} \cdot y^{-1}$.

Changes of nitrate load did not show clear trends during the study period. In waters of the Dunajec the load was intermediate between those recorded in the two other rivers and amounted 821,2 $kg \cdot km^{-2} \cdot y^{-1}$. In the years 1985, 1990 and 1998 nitrate load remained nearly constant and in other years it varied considerably with differences as great as 384 $kg \cdot km^{-2} \cdot y^{-1}$.

Similar relationships between particular catchment basins were also found for $N\text{-}NH_4$ (Fig. 5). Its mean load carried in waters of the Biały Dunajec was 302.7 $kg \cdot km^{-2} \cdot y^{-1}$. The loads tended to decrease with time and were strongly correlated with concentrations (r = 0,99, Table 1). The maximum load of 653,6 $kg \cdot km^{-2} \cdot y^{-1}$ recorded in 1985 was four times higher than that noted in the last study year.

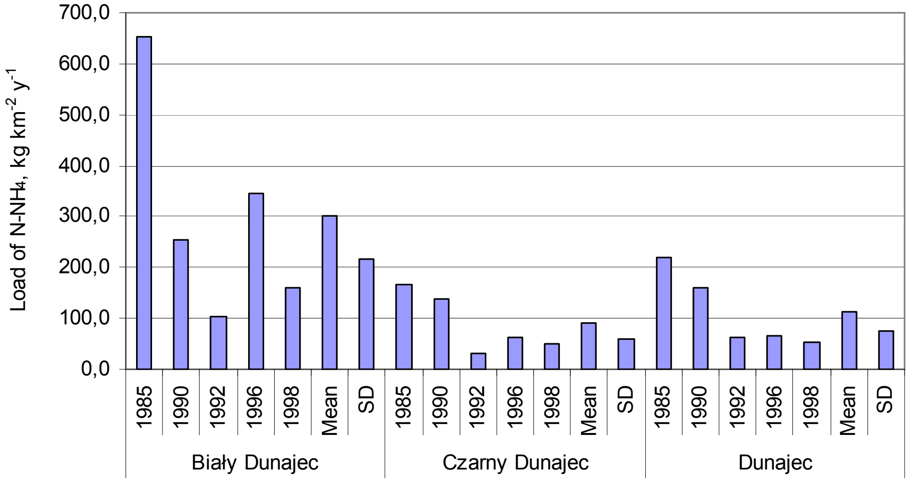

Fig. 5. The loads of N-NH$_4$ discharged in the period 1985–1998 and the mean and standard deviation for the whole study period

Table 1. Correlation coefficients (r) between concentrations and loads of chemical components for the period 1985–1998 (for $n = 5$ and $\alpha = 0.05$ significant $r = \pm 0.95$)

River	Component			
	N-NO$_3$	N-NH$_4$	PO$_4$	BZT$_5$
Biały Dunajec	0.90	0.99	0.98	0.96
Czarny Dunajec	0.17	0.95	0.54	0.48
Dunajec	0.40	0.94	0.78	0.55

In waters of the Czarny Dunajec the load of N-NH$_4$ was 3.4 times lower than that in the Biały Dunajec and amounted 90.1 kg·km^{-2}·y^{-1}. There was a clear tendency of decreasing the load with time. Mean load of ammonium nitrogen carried in waters of the Dunajec was slightly higher (112.6 kg N-NH$_4$·km^{-2}·y^{-1}). In the beginning of the study (1985–1990) it was much smaller ranging from 53.0 to 64.2 kg N-NH$_4$·km^{-2}·y^{-1}.

Analysed catchments were most differentiated in respect to PO$_4$ (Fig. 6). As compared with the Biały Dunajec, mean loads of this nutrient were 9 times lower in the Czarny Dunajec and 5.3 time lower in the Dunajec. The loads in the Biały Dunajec increased with time from 159.2 kg (1985) to 286.5 kg PO$_4$·km^{-2}·y^{-1}.

The loads of PO$_4$ in waters of the Czarny Dunajec remained stable during the study period and averaged 27.2 kg·km^{-2}·y^{-1} (*SD* ±5.5). They were higher by c. 19 kg in the Dunajec and ranged from 36.8 to 61.0 kg PO$_4$·km^{-2}·y^{-1}. Changes of these loads with time showed the reverse tendency to that observed for the Biały Dunajec.

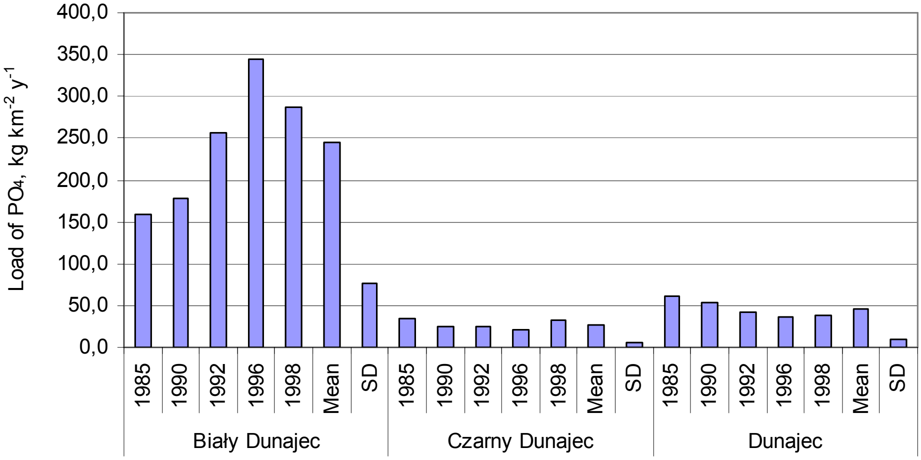

Fig. 6. Loads of PO_4 discharged in particular years of the period 1985–1998 and the mean and standard deviation for the whole study period

The loads of BOD_5 were less variable among studied catchments (Fig. 7). Except for the Biały Dunajec it fell within the range 1283.0–3104.0 kg $O_2 \cdot km^{-2} \cdot y^{-1}$. Definitely highest load of BOD_5 (4189.2 kg $O_2 \cdot km^{-2} \cdot y^{-1}$) was recorded in the beginning of study in the Biały Dunajec. It decreased to 2333.4 kg$\cdot km^{-2} \cdot y^{-1}$ in 1990 to increase again later.

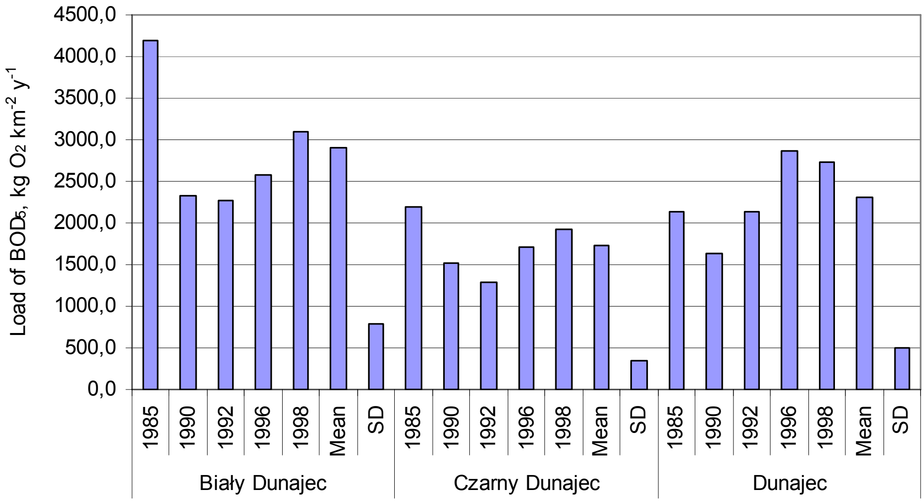

Fig. 7. The loads of BOD_5 discharged in particular years of the period 1985–1998 and the mean and standard deviation for the whole study period

Most even temporal distribution of the loads of BOD_5 was that found in the Czarny Dunajec (Fig. 7). Mean load was 1721.9 kg $O_2 \cdot km^{-2} \cdot y^{-1}$ i.e. 1.3 times lower than the load of BOD_5 recorded in waters of the Biały Dunajec. In both rivers a slight tendency of increasing BOD_5 loads with time was observed.

The mean load of BOD_5 in the Dunajec (2302.0 kg $O_2 \cdot km^{-2} \cdot y^{-1}$) was by c. 600 kg higher than that in the Czarny Dunajec. As in other sampling sites the loads after a decrease in 1990 to 1639.7 kg $O_2 \cdot km^{-2} \cdot y^{-1}$ tended to increase slightly afterwards.

DISCUSSION

Waters of streams forming the Dunajec are of oligotrophic character, particularly in their upper reaches. Concentrations of N-NH_4, N-NO_3 and PO_4 in these waters are low and do not exceed 0.20, 0.10 and 0.02 $mg \cdot dm^{-3}$, respectively (BOMBÓWNA, 1991; KOPACZ, 2003). Flowing downstream through settled areas the waters are posed to human impact and their quality worsens, particularly in respect to N-NH_4 and PO_4. Obtained results demonstrated that the highest concentrations of analysed chemical components were noted in waters of the Biały Dunajec, the river flowing through most populated and most frequently visited areas of the upper Dunajec catchment basin (SMOROŃ, TWARDY, 2001; 2003; 2004).

An increase of the PO_4 loads in waters of the Biały Dunajec could be also associated with increasing number of sewage treatment plants functioning there. RACZAK (2002) when studying surface waters of the Czorsztyn Reservoir catchment basin found highest nutrient (particularly orthophosphate) concentrations in streams that received treated sewage effluents.

Waters flowing from agricultural catchment of the Czarny Dunajec were of the best quality; concentrations of N-NH_4 and PO_4 were not much higher than those observed in the Tatra brooks. The Dunajec in Krościenko carried waters of better quality than the Biały Dunajec – apparently a result of mixing with cleaner waters of its tributaries and due to self-purification of the surface running waters. Waters of the Czarny Dunajec fell within the I–II class of water quality, those in other catchments – to the I–III class as far as analysed components were concerned (Rozporządzenie…, 2004).

The differences between catchments in unit loads of some components resulted from different concentrations since the discharge from studied catchments did not differ so much. The differences in discharge were 22.2 $dm^3 \cdot s^{-1} \cdot km^{-2}$ on average (with the extreme values of 20.8 – in the Czarny Dunajec to 24,8 $dm^3 \cdot s^{-1} \cdot km^{-2}$ – in the Biały Dunajec). This was particularly true for N-NH_4, PO_4 and BOD_5 whose concentrations were significantly correlated with loads. Total load of nitrogen from both agriculture and permanent inhabitants amounted from 62.7 (in the catchments of the Czarny Dunajec and Dunajec) to 91.4 kg $N \cdot ha^{-1} \cdot y^{-1}$

(the catchment of the Biały Dunajec). Respective figures for phosphorus were 18.5 and 19,8 kg P·ha^{-1}·y^{-1} (SMOROŃ, TWARDY, 2004). Mineral and natural fertilisers contributed most to the total nitrogen load in the catchment basins of the Biały Dunajec (88.0%), Dunajec (90.9%) and Czarny Dunajec (94.6%). The rest of nitrogen loads originated from permanent inhabitants. Similarly, both fertilisers contributed most phosphorus to its total load (90.2, 93.0 and 95.6%, respectively). Domestic sewage delivered 5.4% of the total N load and 4.4% of the total P load carried in waters of the Czarny Dunajec. The contribution of sewage input to the total loads recorded in the Dunajec was 9.1% N and 7.0% P and in the Biały Dunajec – 12.0% N and 9.8% P. Thus, one might assume that substantially higher PO_4 loads in the catchment basin of the Biały Dunajec (in relation to the Czarny Dunajec) came from domestic sewage from numerous tourists. This happened in spite of the fact that only less than 5% of permanent inhabitants of the Czarny Dunajec catchment basin delivered their waste waters to treatment plants while the respective figure for the Biały Dunajec was 46% i.e. c. 9 times more.

CONCLUSIONS

The following conclusions can be drawn from presented study:

1. In the years 1985–1998 water quality of the upper Dunajec improved in respect to NH_4 N-NO_3 and PO_4. This was particularly true for waters of the Czarny Dunajec and Dunajec in the section at Krościenko.

2. Highest concentrations and loads of analysed components were noted in waters of the Biały Dunajec. This was probably a result of high population density, improper water and waste water management and from intensive tourism.

3. One of the reasons generating pollution in the Biały Dunajec catchment basin is the technical infrastructure unfit to handle seasonally variable tourist activity.

4. The improvement of water quality in the Czarny Dunajec catchment basin is associated with a switch to environmental friendly land use including restrictions of even abandonment of its exploitation.

5. Tourist impact on natural environment should be a matter of detailed studies with particular focus on surface waters.

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STRESZCZENIE

Stężenia i ładunki N-NO_3, N-NH_4, PO_4 oraz BZT_5 w wodach górnego Dunajca (w latach 1985–1998)

Słowa kluczowe: *ładunki składników N-NO_3, N-NH_4, PO_4, przepływ SSQ, wody powierzchniowe*

W pracy przedstawiono wielkość ładunków N-NO_3, N-NH_4, PO_4 oraz BZT_5 w wodach powierzchniowych zlewni górnego Dunajca (po przekrój w Krościenku) w okresie 1985–1998. Scharakteryzowano jakość wód zlewni Białego Dunajca (punkt w Szaflarach), Czarnego Dunajca (punkt w Ludźmierzu), a także Dunajca – przekrój w Krościenku. Na podstawie wartości średnich rocznych przepływów *SQ* oraz stężeń badanych składników w wodach wymienionych rzek obliczono roczny ich ładunek wynoszony z tego obszaru, przeliczając go na km^2 zlewni. W wodzie Białego Dunajca stężenie N-NO_3 było ponad dwukrotnie, a fosforanów nawet siedmiokrotnie większe niż w Czarnym Dunajcu i Dunajcu. Jest to powodowane zróżnicowaną gęstością zaludnienia, znaczną liczbą osób czasowo przebywających w celach turystyczno-wypoczynkowych, a także niskim poziomem infrastruktury wodno-ściekowej.

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