# Original Research

# Water Quality Changes in the Upper Dunajec Watershed, Southern Poland

E. Szalińska<sup>1\*</sup>, J. Dominik<sup>2</sup>

<sup>1</sup>Institute of Water Supply and Environmental Protection, Kraków University of Technology, Warszawska 24, 31-940 Kraków, Poland <sup>2</sup>Insitute F.-A. Forel, University of Geneva, Versoix, Switzerland

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#### Abstract

Water quality data from the upper Dunajec watershed collected by the state monitoring service in the last 25 years (1977-2003) were examined to asses the evolution of water quality indicators and evaluate the limnological status of the recently constructed Czorsztyn reservoir. The characterization of the watershed and its hydrology is followed by the presentation of physico-chemical and some biological descriptors. The discussion emphasises the temporal trends and links between various observations. It has been concluded that the deterioration of physico-chemical water quality of the upper Dunajec river observed between 1977 and 1988 has been partly reversed due to the construction of wastewater treatment plants and possibly due to the collapse of economic development in 1989.

Keywords: Czorsztyn reservoir, monitoring, phosphorus, upper Dunajec watershed, water quality

#### Introduction

The upper Dunajec river watershed (southern Poland) is valuable for its unique landscape and treasured natural resources. Previous studies on aquatic issues in that watershed have been published in the 1960s [1, 2] or have been limited to specific problems [3, 4]. An extensive source of information about the water quality (from 1977) is data gathered by the Voivodship Inspectorate for Environmental Protection (WIOŚ), conducting state monitoring, but it has never been used for determining long-term trends in the level of contamination in that region.

The goal of this paper is to assess temporal water quality changes of the Czorsztyn reservoir in the context of watershed management impact, using the data collected by WIOŚ in the last 25 years. The assessment should allow us to identify necessary improvements in monitoring and management strategies in order to obtain acceptable water quality in the reservoir.

#### **Material and Methods**

The upper Dunajec watershed is located at the contact between two morphological units of the Western Carpathians (southern Poland). In the north, there are the Gorce Mountains and a range of the Lubań belonging to the Outer Carpathians. In the south, the Nowy Targ valley closes the Inner Carpathians [5]. Between these two units rises the Pieniny Klippen Belt.

The Flysh formation of Carpathian units is composed of Magura and sub-Magura shales and sandstones (Gorce) and sandstones and shales of the Zakopane and Chochołów formations. Limestones, marls, shales and sandstones are the dominant type of rock in the Pieniny Klippen Belt [1]. The mountain climate is characterized by low mean annual temperatures (0-5°C), the mean annual precipitation in the range of 800 to 1200 mm [6].

The total number of permanent inhabitants in the whole upper Dunajec watershed is about 140,000. A strong economic development took place in the region in

<sup>\*</sup>Corresponding author; e-mail: szalinska@wis.pk.edu.pl

the 1970s and '80s. After the political changes in Poland in 1989, and the collapse of the economy, this tendency abruptly reversed and was followed by a slow recovery. Nowadays this is a region with only modest industrialization and urbanization. Its historic, administrative and economic centre is Nowy Targ city (33,600 inhabitants). Agriculture and animal breeding provides most employment. The oldest traditions are maintained by sheep farming and tannery crafts. The cultivable land fertilized with organic manure and artificial fertilizers constitutes more than 60% of total area [7]. The number of tourists is estimated at 600,000 per year and, at the peak season, about 800 per day stay in the Czorsztyn reservoir region.

Nowy Targ and small settlements by the Czorsztyn reservoir are supplied with potable water mainly from surface water (Biały Dunajec) and partially from ground-water [8]. Despite existing infrastructure, the municipal wastewater treatment plant (WWTP) located in Nowy Targ and 11 local WWTPs, wastewater management in the reservoir watershed is still not adequate. Uncontrolled wastewater discharge and surface run-off deteriorate the quality of the surface water used for drinking purposes.

Also, tannery wastewater management in the region is unsatisfactory. A significant number of small tanneries located in the reservoir neighbourhood discharge pre-treated or raw wastewater into local sewers or directly into streams [9]. Tanning technology is based on chromium compounds which periodically contaminate surface water and river sediments, especially in the autumn-winter season when tanned skin production is at its maximum.

#### Hydrological Characteristics

The Dunajec river originates from the confluence of two main streams: the Biały Dunajec and the Czarny Dunajec. The most upstream gauge is located at the Kowaniec cross-section close to Nowy Targ city. An earthen dam was constructed on the Dunajec river at 173.3 km from the outlet to the Vistula river and the Czorsztyn reservoir was filled in 1997. Built for reducing the impact of seasonal flooding, it is also used for power generation and for recreation. The mean annual flow (1951-80) in the Kowaniec cross section was 13.9 m<sup>3</sup>s<sup>-1</sup> and in the present dam cross-section (Czorsztyn) was 23.8 m<sup>3</sup>s<sup>-1</sup> [10]. Great diversity in the flow was observed in individual months, with annual maximum at Kowaniec above 20 m<sup>3</sup>s<sup>-1</sup>, recorded in April (snow melting) and June (heavy rainfall) and a minimum, in the range of 6.6-7.8 m<sup>3</sup>s<sup>-1</sup>, in January and February.

The second reservoir tributary is the Białka Tatrzańska river (the former right-bank tributary of the Dunajec river). The mean annual (1996-99) flow in the Trybsz crosssection is 7 m<sup>3</sup>s<sup>-1</sup> and the seasonal variability similar to that observed in the Dunajec river. In the northern part the reservoir is joined by numerous creeks draining slopes of the Gorce Mts. In the southern part, the minor tributary is the Niedziczanka (2.1 m<sup>3</sup>s<sup>-1</sup>) stream, which flows to the compensation reservoir (Sromowce Wyżne).

The total area of the Czorsztyn reservoir, at normal water level, is 1051 ha with the water level at 529.0 m above sea level (a.s.l.). The ratio of the watershed to reservoir areas is just above 100, which is a typical ratio for reservoirs outside the arid zones [11]. The capacity of the reservoir is 168.6 millions m<sup>3</sup>. The maximum depth at normal filling level is 45 m and the mean depth 22 m. Water intake to the power plant is situated at a depth of 19-23 m at normal water level. During stratification period the intake is thus most of the time located below thermocline. At the mean annual total inflow 27.9 m<sup>3</sup>s<sup>-1</sup> (a value extrapolated from the measurements at Kowaniec, considering the increase in watershed area) the residence time in the reservoir is 70 days, but at high water inflow (April-June) total water exchange in 5 days is theoretically possible.

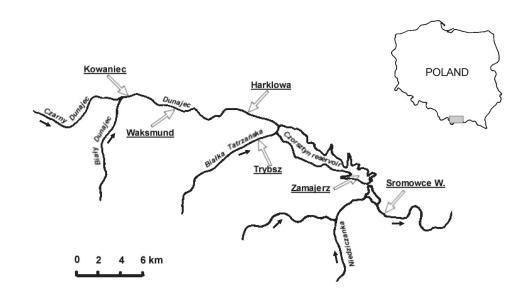


Fig. 1. Localizations of the studied area and investigated cross-sections in the Czorsztyn reservoir region.

Water body	Cross section	Terms of investigations
Białka river	Dębno	1977-84, 1988, 1990-92
Dunajec river	Kowaniec Waksmund Harklowa Sromowce Wyżne	1993-95, 1997-03 1977-85, 1988-89, 1995-99 1977-82, 1984, 1988-03 1997-03
Czorsztyn reservoir	Zamajerz	1999-03

Table 1. Documented periods of Voivodship Inspectorate for Environmental Protection investigations in the Czorsztyn reservoir region.

## Data on Chemical Composition of Water and Their Statistical Treatment

Description of chemical composition of water is based on environmental quality data from 25 years made available by the WIOŚ to authors and from other sources [1, 2, 3, 4].

Data were obtained from the Dunajec river upstream from the reservoir (Kowaniec, Waksmund and Harklowa cross-section), the Białka river (Dębno cross-section), the Czorsztyn reservoir (Zamajerz harbour) and the Dunajec river downstream from the reservoir (Sromowce Wyżne cross-section) (Fig. 1).

The data set is neither continuous nor synchronous for various cross-sections (Table 1). The frequency of river sampling varied from 4 to 24 times per year depending on the cross-section and period. Measurements in the Czorsztyn reservoir were carried out only at one sampling point, three times per year. All parameters were determined according to the standards and methodology used in the Inspectorate for Environmental Protection [12]. The quality assurance programme, in accordance with ISO standards, was introduced by WIOS in the nineties. The quality of earlier data was controlled only by internal practices. For determination of interannual trends of particular compound concentrations (described in the part Organic matter and nutrients) the question of validity of comparing means from different years based on the different number of samples per year (24, 12, 6, 4) was considered. Statistical tests were performed for all compared compounds in the Harklowa cross-section using sets of data from 5 consecutive years (1993-97) with 24 discrete samples available. For each year smaller subsets of data were selected with n = 12, 6 and 4, according to the dates of sampling used in other years with a lower frequency of sampling. Whenever the distribution of all 4 sets were accepted as normal with Kolgomorov-Smirnov test, the parametric one-way ANOVA was used. Otherwise ANOVA on ranks was performed with Kruskal-Wallis method. For the set of 24 and 3 subsets in each year the null hypothesis that the samples are taken from the same population cannot be rejected was tested. The comparison of mean annual concentrations for different years calculated on the base of n =24, 12, 6 and 4 samples appeared meaningful for all tested parameters, although the confidence interval for the mean decreases with decreasing n.

### **Results and Discussion**

#### Physico-Chemical Factors

The water temperature usually ranged from 13 to 21°C throughout summer months, owing to the rapid water current that prevented heating of the water. During winter months temperature did not exceed 3°C. Downstream from the reservoir the temperature amplitude during a year was lower than upstream by  $\pm 1$  to  $\pm 5$ °C. During the spring-summer period water temperatures were lower in the Sromowce cross-section than upstream and during autumn-winter months they were higher. This is a result of deep water intake from the reservoir at the power station.

Dissolved oxygen in the running water usually exceeded  $6.0 \text{ O}_2 \text{ mg } \text{I}^{-1}$ . In the Czorsztyn reservoir thermal-oxygen conditions were labile. The stratification was strongly affected by the great inflow variability during spring-summer period, and the pumped-storage work mode of the power plant. Water in the reservoir was generally well oxygenated. The lowest value of  $4.2 \text{ mg O}_2 \text{ mg } \text{I}^{-1}$  was noticed in the bottom layer during summer stratification (45.9 % oxygen saturation).

pH was almost always within the alkaline range, due to the calcareous nature of the geological substratum. Maximum pH values, above 9.0, noted from June to September in the Dunajec cross-sections can be related to the rich development of periphyton on the stony bottom [13]. Electrolytic conductivity was in the range of 110-773  $\mu$ S cm<sup>-1</sup> with maximum values at low flow conditions (December-February).

During snow melting periods and also during summer high flow events the concentration of the total suspended solids upstream from the reservoir were high (above 200 mg l<sup>-1</sup>) while they were usually below 15 mg l<sup>-1</sup> at low flow conditions. Downstream from the reservoir the suspended solid concentrations decreased because of sedimentation in both reservoirs. The mean values of the total suspended solids were  $15 \pm 37$  mg l<sup>-1</sup> and  $7 \pm 6$  mg l<sup>-1</sup> for cross-sections upstream and downstream from the reservoir, respectively (1997-2003).

#### The Ionic Composition of the Water

The ionic composition of the Dunajec and the Białka rivers was typical for the surface water of the Northern Carpathians i.e. a calcium-bicarbonate one. In the whole investigated area the bicarbonates predominated (68-78% of total anions) over sulphates (15-23%) and chlorides (8-11%). The sulphate and chloride concentration level in the Czorsztyn reservoir and downstream from the reservoir decreased as compared to the upstream cross-sections due to dilution, essentially by the Bialka river. Among cations, calcium (66-69% of total cations) and magnesium (22-25%) prevailed over sodium (5-9%) and potassium (1-2%). The percentage balance error was below 10 for all the investigated cross-sections, which is an acceptable error for surface waters [14].

The low iron concentration is characteristic for water in Carpathian streams. The average value in headwaters of 0.05 mg l<sup>-1</sup> [2] increased in the lower reaches of the river, up to 3 mg l<sup>-1</sup> during high water events. When comparing more recent data (1977-92) with previous sets (1962-63), an increase of sulphate and chloride concentration was observed. This can possibly be attributed to the increased wastewater discharge and long-range air pollution transport.

#### Organic Matter and Nutrients

Biochemical oxygen demand (BOD<sub>5</sub>) was taken into consideration as a main index of degradable organic matter content. The mean annual BOD<sub>5</sub> values at the mouth of the Białka river were always below 4.0 mg O<sub>2</sub> l<sup>-1</sup>. For the Dunajec river, upstream from the Czorsztyn reservoir three periods in the distribution of the mean annual BOD<sub>5</sub> values can be distinguished (Fig. 2a). From 1977 to 1988 BOD<sub>5</sub> increased gradually (up to 8 mg O<sub>2</sub> l<sup>-1</sup>), which was related to the significant economic development in the region at that time. A distinct decrease

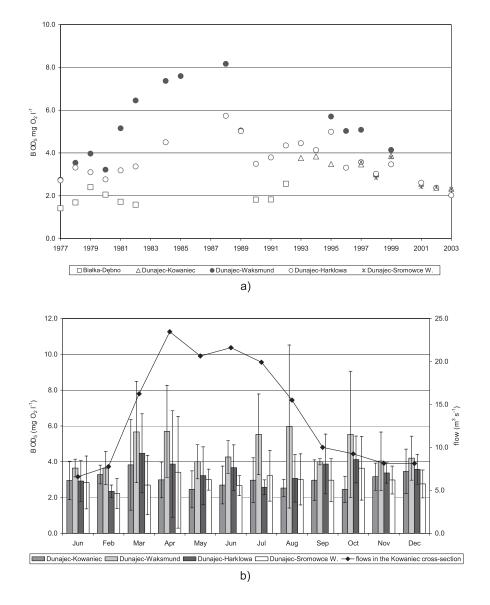


Fig. 2. Distribution of the mean annual (1977-2003) (a) and the mean monthly (1997-2003) (b)  $BOD_5$  values in the cross-sections of the Białka and Dunajec rivers (for the Waksmund cross-section data from 1997-99 were used for monthly means). On the monthly distribution the standard deviations are marked. Line with markers represents distribution of the Dunajec river mean monthly flows for the Kowaniec cross-section.

of the BOD<sub>5</sub> values occurred in 1989, followed by a minor gradual increase during the next five years. Assuming that there is no analytical shift due to restructuring of the monitoring service, the variations in the BOD<sub>5</sub> values might reflect the economic collapse in 1989, followed by a slow recovery. According to data after 1997, the BOD<sub>5</sub> values in the Dunajec river directly upstream and downstream from the Czorsztyn reservoir and in the reservoir were very similar and did not exceed 4 mg O<sub>2</sub> l<sup>-1</sup>. The tendency of BOD<sub>5</sub> decrease after 1997 is possibly related to the improvement of the WWTP network.

The increase of the mean monthly  $BOD_5$  values in March-April (Fig. 2b) can mainly be attributed to surface run-off during spring thaw. The increased values in early autumn (September-October) in the Waksmund and Harklowa cross-sections at low flow, suggest the impact of point sources (for example local tanneries). The BOD<sub>5</sub>

distribution downstream from the reservoir showed a pattern similar to the upstream one, displaced in time owing to the water retention in the reservoir.

The mean annual ammonia concentrations (below 1.0 mg N  $I^{-1}$  for the whole period) show a decrease from the late 1980s. It might be related to the gradual improvement of Biały Dunajec river quality after putting into operation the wastewater treatment plant in its watershed. During the year ammonia concentrations increased in the winter – early spring season (December-April) due to increased discharges of wastewater from the winter sports resorts and slowing down the nitrification process in the winter ter period. The monthly distributions of nitrate (Fig. 3a) and nitrite (Fig. 3b) concentrations showed the opposite trends. In winter, at a low water flow, but also in spring, nitrate shows elevated concentrations at cross-sections upstream from the reservoir. The high concentrations

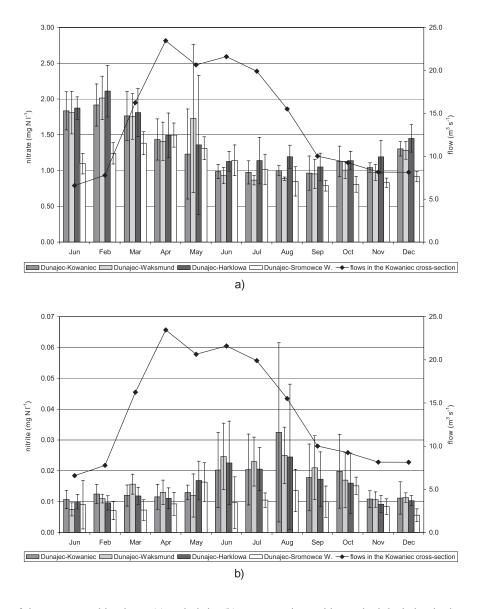


Fig.3. Distribution of the mean monthly nitrate (a) and nitrite (b) concentrations with standard deviation in the cross-sections of the Dunajec river (1997-2003). For the Waksmund cross-section data from 1997-99 were used. Line with markers represents distribution of the Dunajec river mean monthly flows for the Kowaniec cross-section.

in spring can be attributed to the surface run-off during spring thaw. High values of nitrite concentrations (above 0.03 mg N l<sup>-1</sup>) found in the summer months can be attributed to the increased denitrification in sediments, accelerated at higher temperatures [15].

The temporal evolution of total phosphorus concentrations in the Dunajec river at Harklowa and Sromowce Wyżne cross-sections, upstream and downstream from the reservoir, respectively, is shown in Figure 4. The concentrations at the Sromowce Wyżne cross-section are probably a fairly good representation of hypolimnion concentration of total phosphorus in the reservoir, as the water intake for the power plant is usually situated below the thermocline. For the whole period of existence, the reservoir's concentrations are, on average, lower than at Harklowa, demonstrating the retention of phosphorus in the reservoir sediments. The phosphorus loading decreases in the first years after reservoir construction and seems to stabilize in the period 2001-03.

As in a large majority of lakes and reservoirs in temperate climates, primary production in the Czorsztyn reservoir is limited by the availability of phosphorus. The mean atomic N<sub>tot</sub>/P<sub>tot</sub> ratio in the reservoir (73.5 ± 53.4) is higher than in the cross-sections upstream and downstream from the reservoir (45.1 ± 24.4 and 61.4 ± 34.0, respectively). Also, the ionic nitrogen (N-NO<sub>3</sub><sup>-</sup> + N-NH<sub>4</sub><sup>+</sup>) to phosphates (P-PO<sub>4</sub><sup>-3</sup>) ratio is largely in excess of the nitrogen demand of freshwater plants [11]. Phosphorus being the limiting nutrient, the Vollenweider model (here presented in the notation used by Wetzel [16]) can be applied. It has been shown [17, 18] that the total phosphorus concentration in lakes [*P*]<sub>*i*</sub> can be predicted from the mean concentration in tributaries [*P*]<sub>*i*</sub>, and mean residence times of water ( $\tau_{u}$ ) and phosphorus ( $\tau_{u}$ ) as follows:

$$\left[P\right]_{\lambda} = \left[P\right]_{i} \frac{\tau_{p}}{\tau_{w}}$$

As the mean residence time of phosphorus in a lake in not easy to measure, the quotient  $(\tau_p/\tau_w)$  can statistically be approximated as:

$$\frac{\tau_p}{\tau_w} = \frac{1}{1 + \sqrt{\tau_w}}$$

Clearly, this simple model relating to loading concentrations in lakes is not always readily applicable to individual lakes or reservoirs, but it is generally recognized to be a useful and simple approximation of reality [16]. With the mean total phosphorus concentration in the Dunajec river at the Harklowa cross-section for the period 2001-03 of 0.047 mg l<sup>-1</sup> and mean water residence time of 70 days, Vollenweider's model predicts a mean lake concentration of total phosphorus of 0.033 mg l<sup>-1</sup>, which is only marginally higher than the mean concentration observed at the Sromowce W. cross-section (0.031 mg l<sup>-1</sup>). As the Dunajec river supplies about 2/3 of water to the reservoir and the Białka river the remaining 1/3 (rough estimation neglecting other reservoir tributaries), the calculation can be refined assuming the current mean phosphate concentration in the Białka river the same as that measured in the period 1990-1992 (last three years of systematic survey). The mean concentration in tributaries  $[P]_i$  is then obtained from the relation between phosphates and total phosphorus measured at the Harklowa cross-section (r = 0.71). The calculated mean input concentrations would then decrease to 0.036 mg l<sup>-1</sup> and the predicted concentration in the reservoir to  $[P]_{1} = 0.025 \text{ mg } l^{-1}$ , only slightly less than the observed concentration at Sromowce W. This estimation matches reasonably well the mean concentra-

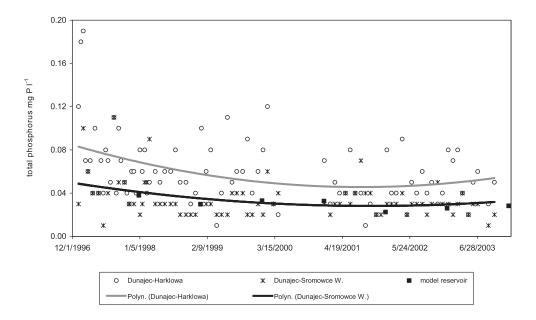


Fig. 4. Temporal evolution of total phosphorous concentrations in the Dunajec river at the Harklowa and Sromowce Wyżne cross-sections from 1997-2003 (trend lines are second degree polynomial fit to the data). Full squares show the predicted yearly mean concentrations in the reservoir according to Vollenweider's model based on estimated mean loading from the Dunajec and Białka rivers (see text).

tions measured in the period 2001-03 in the reservoir (Zamajerz harbour) of 0.026 and 0.030 mg  $l^{-1}$  in surface and bottom water, respectively.

The demonstrated applicability of Vollenweider's model enables us to estimate the theoretical phosphorus concentration in the lake. The phosphorus loading would then be maintained at the level observed in the 1980s, prior to the economic collapse in the watershed and the construction of wastewater treatment plants. As only phosphate concentrations were measured at that time, the estimation of total phosphorus was obtained from a PO<sub>4</sub>/ P<sub>tot</sub> linear relationship established for more recent measurements. If the mean total phosphorus concentration of about 0.077 mg l-1 in the Dunajec river is not reduced to the present level, one could expect the phosphorus concentration in the reservoir of about 0.054 mg l<sup>-1</sup>. At this level of phosphorus concentration the probability that the reservoir turns to eutrophic conditions would be relatively high. This clearly demonstrates that the construction of the WWTPs was absolutely necessary to prevent eutrophication of the reservoir.

#### Heavy Metals

Among heavy metals, chromium is the contaminant of concern in the Czorsztyn reservoir area. During the intensive activity of local tanneries (November through January) the highest total chromium concentration exceeded 0.08 mg l<sup>-1</sup> in the Dunajec river (the Waksmund cross-section) [4]. Chromium introduced to the river during the tannery production season is temporarily accumulated in bed sediments in the region of discharges. During flood events these sediments are flushed out into the Czorsztyn reservoir where they are trapped. As chromium occurs mainly as Cr(III) and is transported largely in the particular and colloidal forms [19, 20, 21] its availability to phytoplankton is limited. Nevertheless, the algal bioassays with aqueous extracts from highly polluted sediments collected at a tannery canal demonstrated potential toxicity of chromium [22]. Furthermore, the impact of chromium contamination on the benthic community is still unknown.

The concentrations of other investigated metals in water, such as zinc, copper, nickel and lead are low, in the range of a few micrograms per litre.

#### **Biological Indices**

Among biological indices that describe water quality, chlorophyll *a* concentration, Saprobic index and faecal coliform bacteria index were taken into consideration.

In the Czorsztyn reservoir the chlorophyll *a* concentration varied from 1.6 to 42.0  $\mu$ g l<sup>-1</sup> (1999-2003). In flowing water the concentrations were lower, in the range of 0.9 – 35.0  $\mu$ g l<sup>-1</sup> for the Dunajec river upstream from the reservoir and 0.9 – 13.6  $\mu$ g l<sup>-1</sup> downstream.

At the present total P loading, statistically predicted chlorophyll a, mean yearly concentration in the reservoir (Vollenweider 1976, using constants 0.55 and 0.76, as proposed by Wetzel 2001) is 6.4  $\mu$ g l<sup>-1</sup>. This is quite close to the observed mean concentration at Zamajerz harbour  $(8.2 \ \mu g l^{-1})$ , although the later value is based only on a very limited number of measurements at the station situated close to the lake shore, and should be refined. The model calculations suggest that at the loading level of the 1980s, the mean chlorophyll a concentrations would be above 11.0  $\mu$ g l<sup>-1</sup>, close to the mean value for eutrophic lakes. Using a largely accepted classification of a lake trophy, based on a few parameters (Wetzel [16] as modified from Vollenweider [17]), the present status of the Czorsztyn reservoirs can be considered as typically mesotrophic. This strongly suggests that a very careful phosphorus control in the watershed is needed to avoid its transition to the eutrophic state.

Intensified use of the watershed for sheep and cattle grazing coupled with untreated wastewater discharge led to a deterioration of water sanitary quality. For unpolluted water the faecal coliforms occur at a level of 20-200 bacteria per 100 ml. In all investigated cross-sections of the Dunajec river the coli titre ranged from 4 (about 25 bacteria per 100 ml) to 0.000004 (about 25,000,000 bacteria per 100 ml). Maximum bacteria numbers were detected during thaw periods and high water events due to rainfall. The sanitary quality of the Białka river was the best. Even during the high flow conditions the coli titre did not fall below 0.04 and throughout the rest of the time exceeded 1.0.

#### Conclusions

The overall water quality assessment, based on the data sequences obtained from WIOS, revealed that the range and the distribution of contamination in the Dunajec river indicates the strong effect of both surface runoff and point sources. The upper Dunajec watershed has a distinctly mountainous character. Thaw (March - April) and high rainfall (June – July) play an important role in the water balance of rivers and streams. The surface runoff in these periods affects the load of suspension, organic matter and nutrients. Economic development in the 1970s and '80s brought about the increase of mean annual values of contamination indices (BOD, ammonia, phosphates). The water quality in the watershed was clearly improved due to the starting up of the high capacity wastewater treatment plants and a number of smaller plants before filling the Czorsztyn reservoir.

Calculations performed using Vollenweider's model show that it is crucial to maintain the phosphorus loading at a low level and, if possible, suppress the total phosphorus concentration in rivers below 0.03 mg l<sup>-1</sup>. The low mean concentration of total phosphorus in the less polluted Białka river clearly shows that the abatement below 0.03 mg l<sup>-1</sup> is certainly possible and can be tentatively considered as a target value. The accumulation of phosphorus in reservoir sediments may become more important as an internal source than it is at present. However, with the available data it is exceedingly difficult to predict a "safe" level of phosphorus loading, as Vollenweider's model, with all its merits, should not be considered a priori, as generally valid. The model should be tested by monitoring a number of critical parameters in the reservoir, such as phosphorus, chlorophyll a and oxygen concentration profiles, primary production and transparency. Furthermore, monitoring of the phosphorus concentration should be coupled with discharge measurements at the same point to obtain more precise load estimation. According to the obtained data, some improvements can be observed in the last years. It is possible that the improvement of water quality might be not sufficient and more attention should be paid to the monitoring in the Czorsztyn reservoir watershed. Also, contaminant profiles in reservoir water and sediment survey could be very useful for understanding the reservoir processes.

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