Chapter 17

Processes and the Resulting Water Quality in the Medium-Size Turawa Storage Reservoir after 60-Year Usage

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Additional information is available at the end of the chapter

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Abstract

The characteristics of water in the Turawa reservoir, one of the important storage reservoirs in Poland, were thoroughly studied. The reservoir and also the rivers flowing into the reservoir were monitored in the period 2004–2006 with respect to the basic physico-chemical parameters determining the quality of water such as water temperature, specific conductance, pH, biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD_{Mn}), water hardness, content of typical ions (sodium, potassium, sulphates, phosphates and chlorides), heavy metals, and so on. The observed seasonal and long-term changes of the parameters measured were discussed and the processes responsible for the changes suggested. The causes of the observed deterioration of the ecological status of the Turawa reservoir were given and the remedial operations proposed. The latter included improvement in the management of solid wastes and wastewater in the area, reducing the runoff of nutrients in the catchment, decrease in discharge of pollutants into the rivers flowing into the reservoir, removal of bottom sediments and also increasing the average water table and decreasing its fluctuations. The effect of the remedial operations will be further studied.

Keywords: Turawa reservoir, physico-chemical parameters, changes of water characteristics, remediation propositions, pollution sources

1. Introduction

The resources of surface waters in Poland are relatively low, not equally distributed and characterized by seasonal variability. The total annual runoff is about 57 km^3 of water, which is equal to 1600 m^3/person—this is a third of the European average runoff per person (statistic data). In order to improve the availability of water, quite a number of storage water reservoirs have been built in different parts of the country. Generally, water storage behind large dams is applied whereby the water is used for power generation, municipal water supply and flood control. Large storage reservoirs with controlled discharge provide larger amounts of water for periods of drought or low flow in the streams. In Poland, there are about 100 reservoirs characterized by a capacity of over 1 million m^3 each. The total storage capacity of the Polish reservoirs is about 4000 million m^3, which constitutes about 6% of the annual runoff (statistic data). Unfortunately, this storage capacity has not been sufficient up to now. Moreover, the strong anthropopressure still observed makes that the water quality is not satisfactory in many cases. So, the efforts are being undertaken to increase water retention and eliminate or, at least, strongly decrease water pollution.

One of the larger water reservoirs in Poland is the Turawa reservoir, operated since 1948. It is used to drive a hydroelectric power plant, as a source of water for municipal water supply systems, and also for recreation.

The Turawa reservoir is situated between 50°42′27″ and 50°44′32″ north latitude and 18°04′51″ and 18°10′59″ east longitude in Mała Panew Valley, which is the part of Równina Opolska (Opole Plain) (**Figure 1**).

Figure 1. Localization of the Turawa reservoir in Poland (Terra/Modis NASA).

It is situated on the Mała Panew river 16 km away from where it flows into the Odra river. The two other smaller rivers supplying the reservoir with water are the Libawa and the Rosa. The participation of these rivers in the surface water inflow to the Turawa reservoir is 87, 9 and 4%, respectively.

Morphometrical parameters of the Turawa reservoir are as follows: capacity, 95.5 hm^3; surface area, 20.9 km^2; length, 7.4 km; maximum width, 3.45 km; average width, 2.26 km; length of the shore line, 29.5 km; maximum depth, 13.68 m and average depth, 4.70 m. The water turnover time in the Turawa reservoir in the years 1996–2005 was 59 days on average: the shortest 37 days in 2001 and the longest 87 days in 2003. The turnover time was calculated as the quotient of the sum of water evaporating, water exchanged with catchment and water that flows out of the reservoir divided by the annual average capacity of the reservoir. The water turnover time is the theoretical value, which allows for the approximate assessment of the process. On the basis of this parameter, the Turawa reservoir can be classified as a high-flow water body.

The Turawa reservoir plays an important role in Poland, but due to the strong agricultural and industrial anthropopressure its water quality in the studied period was rather poor. The quality of water in the Turawa reservoir is determined by the composition of the water of the rivers flowing into the reservoir, that is, the Mała Panew river, the Libawa river and the Rosa river and also by the processes proceeding in the reservoir itself. The Mała Panew is the most polluted of the above-mentioned rivers; it carries industrial, municipal and agricultural pollutants. The largest amounts of wastewater are discharged from the several cities in the neighbourhood of the reservoir [1, 2].

The main source of nitrogen and phosphorous compounds is the application of fertilizers in arable land in the catchment of the Mała Panew and the Libawa rivers.

Any pollution prevention and remedial programmes need the determination of the large number of physico-chemical parameters characterizing water quality and the dynamics of the changes of these parameters.

2. Measured parameters and sampling points

All typical parameters generally used to classify surface waters were measured, mostly in the recognized laboratories of water analysis by means of recommended procedures and some on-site using specialized measuring instrumentation. Laboratory-measured parameters are given in **Table 1** (parameters typical for water purity classification).

The measurements were made for 20 sampling points situated in the selected sites of the reservoir, the rivers flowing into the reservoir, namely the Mała Panew, the Libawa and the Rosa, the river flowing out of the reservoir, that is, the Mała Panew, and the small lakes in the neighbourhood of the reservoir. The points for on-site measurements and for collecting samples for laboratory analysis are presented in **Figure 2**.

Specific conductance was measured on-site using conductance metre whose accuracy was 0.1 $\mu S\ cm^{-1}$. For oxygen content in water, the oxygen metre, enabling to carry out measurements up to the depth of 20 m, was used. Temperature was measured with the use of a mercury thermometer and also thermometers being integral parts of pH, oxygen and conductance metres. To determine water transparency, Secchi disk was applied. Bathymetric measurements were performed by means of a Lowrance sonar and an acoustic Doppler current profiler.

Parameter	**Parameter (AAS)**
Chemical oxygen demand (COD_{Mn})	Magnesium (Mg)
Biochemical oxygen (BOD_5)	Manganese (Mn)
Total hardness (TH)	Iron (Fe)
Calcium (Ca^{2+})	Cobalt (Co)
Magnesium (Mg^{2+})	Nickel (Ni)
Alkalinity (HCO_3^-)	Copper (Cu)
Chloride (Cl^-)	Zinc (Zn)
Sulphate (SO_4^{3-})	Cadmium (Cd)
Phosphate (PO_4^{3-})	Lead (Pb)
Nitrate (NO_3^-)	
Sodium (Na^+)	**Parameter**
Potassium (K^+)	Cyanides
Escherichia coli	PAH (total)
Total organic carbon	Total Phosphorous
Ammonia nitrogen	Total dissolved matter
Nitrogen by Kjeldahl	Phenol index
Total nitrogen	Anionic surfactants
Fluorides	Mineral oil index
Total alkalinity	

Table 1. Laboratory-measured parameters.

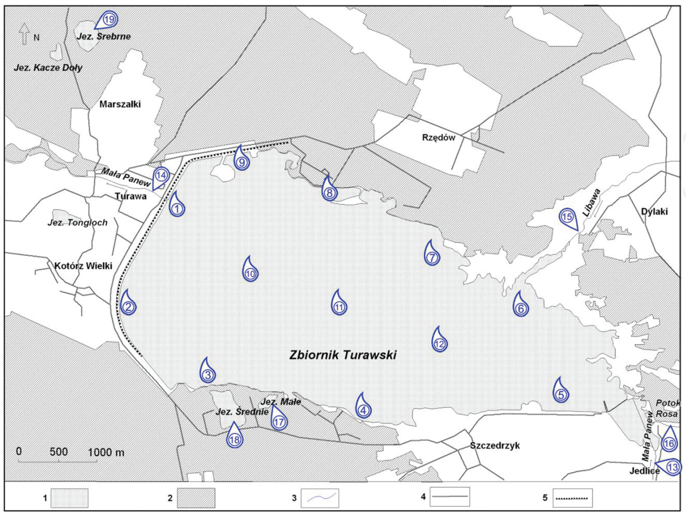

Figure 2. Location of the points for collecting samples for physico-chemical measurements: Geographical features: 1, water reservoirs: Jez. - lake and Zbiornik Turawski—the Turawa reservoir; 2, forests; 3, rivers; 4, roads; 5, dam.

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Bathymetric measurements have shown that the reservoir is the deepest in the vicinity of the dam and the shallowest at the inflows of the rivers into the reservoir: the Mała Panew, the Libawa and the Rosa (**Figure 3**).

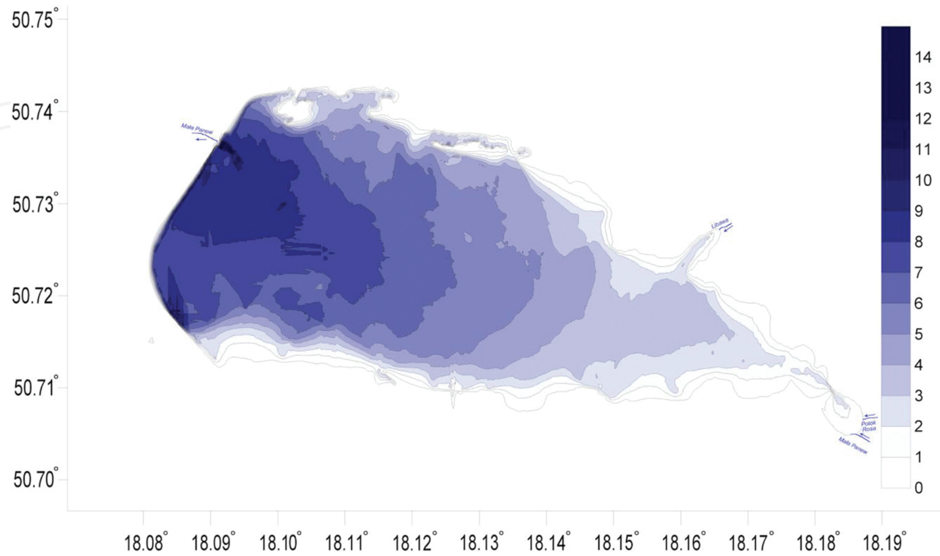

Figure 3. Bathymetric chart of the Turawa reservoir.

3. Water temperature in the reservoir

The water temperature and its fluctuations are important characteristics of storage reservoirs. In the areas characterized by well-defined cyclic temperature changes, the diurnal and seasonal temperature changes of surface water are typical. Thermal conditions of water reservoir are determined by climate (temperature of air, insolation, direction and speed of wind) and reservoir morphology, subsoil type and vegetation [3]. Water temperature can also be influenced by anthropogenic factors.

In the case of the Turawa reservoir, the water temperature changes in a wide range. It depends mainly on air temperature. In 2004–2006, the average water temperature was relatively well correlated with the changes of average monthly air temperature (correlation coefficient of 0.9).

In a year cycle, there are two periods of relatively stable temperature, winter season and summer season, and also two periods characterized by large water temperature changes, spring and winter seasons. The monthly minimum temperatures in the range of 0.6–0.8°C were observed in the period from December to February. The maximum temperatures ranging from 23.1 to 25.4°C were measured in July and August. In the period discussed, the lowest temperature was 0.3°C (January 2004) while the highest was 26.7°C in July 2006.

The changes of the limits of thermal layers and periods of water circulation and stagnation were also studied. Spring circulation starts after ice melts off and is characterized by temperature increase (from 0°C). Heavier water moves downwards while colder water from the bottom layer moves up resulting in water mixing and constant temperature in a vertical profile [4].

The period of summer water stagnation is characterized by temperature drop with depth. This is typical water stratification whereby the upper layer of the highest temperature close to air temperature is epilimnion and the coldest bottom layer is hypolimnion. The water between these two layers is metalimnion. Due to the small depth of the reservoir (in summer rarely more than 10 m in the deepest point) and intensive wind mixing in summer stagnation period thermal stratification was not observed—vertical temperature difference did not exceed 4°C (**Figure 4**).

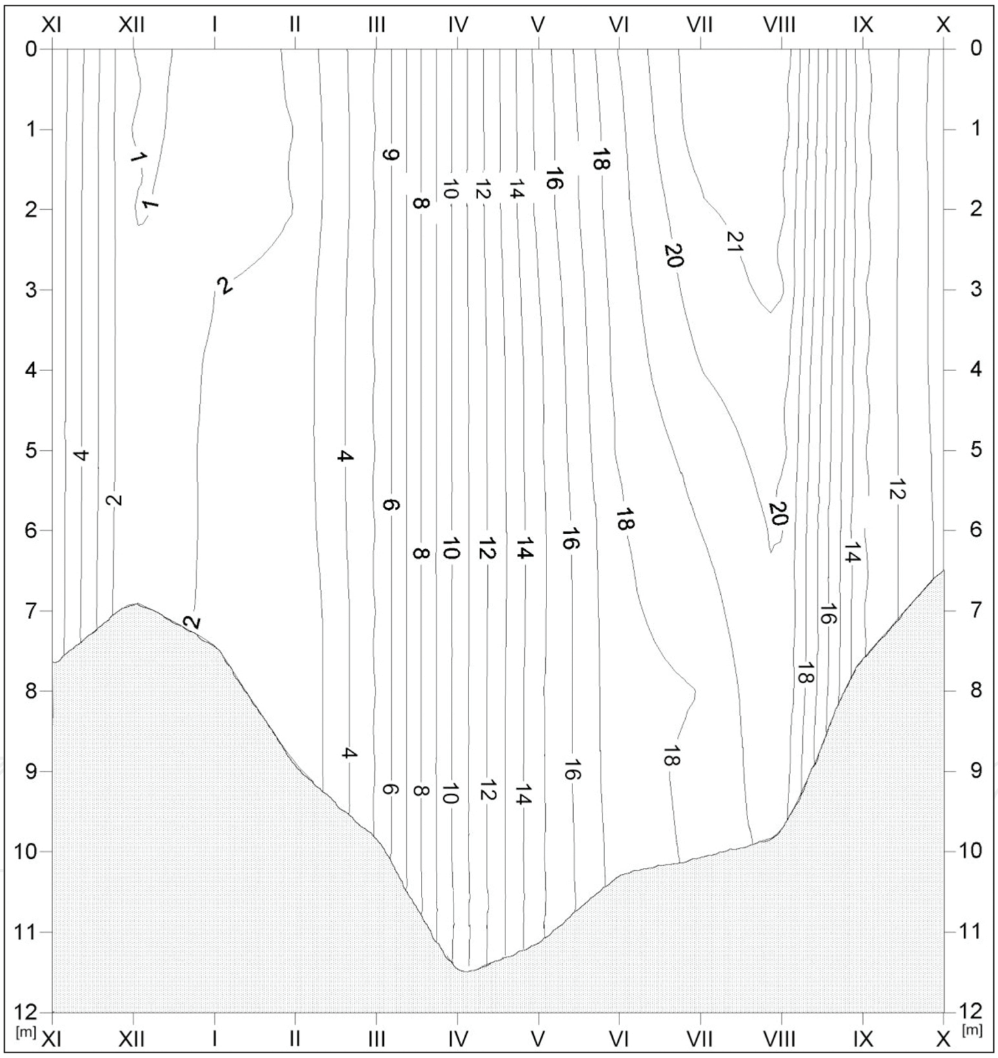

Figure 4. Changes in water temperature in the Turawa reservoir in the hydrological year 2004—vertical profile: 50°44′10.28″N, 18°05′30.22″E.

At the beginning of September, the period of autumn circulation starts in the Turawa reservoir. Due to cooling of surface layer, wind and convective mixing, the difference between the water

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temperature of epilimnion and hypolimnion in storage reservoirs decreases [5]. In the case of the Turawa reservoir, the process of decreasing difference in temperature was accelerated by intensive water outflow in the period from September to December. The water level dropped by 2.5 m and the water volume approximately by 30 million m^3. The process of water cooling ended when the temperature dropped to 4°C in the whole thermal profile, what for the Turawa reservoir was at the turn of November and December. From December to February (hydrological year 2004) or to March (hydrological years 2005 and 2006), winter stagnation occurred. In the deepest parts of the Turawa reservoir, water temperature was in the range of 2–2.7°C, while directly under ice layer it was 0.8°C.

In fact, summer stratification did not occur in the Turawa reservoir—the average water temperature was high and ranged from 20 to 21.8°C, whereas in winter it was in the range of 0.8–2.0°C. The annual average water temperature for the whole reservoir changed from 10.1 to 10.7°C. Thermal variability of the reservoir or the ratio of maximum temperature to minimum temperature reached the value of 26. In the hydrological years 2004–2006, the thermal conditions of the reservoir were strongly influenced by fluctuations of water level and the corresponding large changes of the volume of water from about 16 to 91 million m^3. The relatively small average depth of the Turawa reservoir favours wind mixing.

The interesting characteristics of the Turawa reservoir are water-freezing phenomena. The earliest time ice cover appeared was the end of November while the latest time its disappearance was the beginning of April; on average, it was the second half of December and the middle of March, respectively. The ice cover disappeared first in the coastal zone, most likely due to higher absorption of heat by land masses and intensive supply of surface and ground water.

The annual length of time the Turawa reservoir was covered with ice varied within a wide range. In the studied period, it changed from 18 days in 1994 to 106 days in 1984, on average 61 days. There were also large differences in the thickness of ice cover, an annual average cover ranged from 6 cm in 1988 to 26 cm in 1996. Due to the formation of ice cover, anthropogenic storage reservoirs, including the Turawa reservoir, can be used for recreation, too.

4. Oxygen saturation

The oxygen dissolved in surface water comes mainly from the atmosphere and photosynthesis processes; its content is one of the most important parameters characterizing the quality of water. Oxygen is necessary for the life of fishes and other water animals. The oxygen content depends on the physical (temperature) parameters and on biological processes. Water pollution generally results in drop of oxygen content. In the hydrological years 2004–2006, the Turawa reservoir water saturation with oxygen was typical (60–100%) from autumn to spring with the highest values in winter (**Figure 5**). In that period, the average oxygen saturation in vertical profile ranged from 58 to 102%.

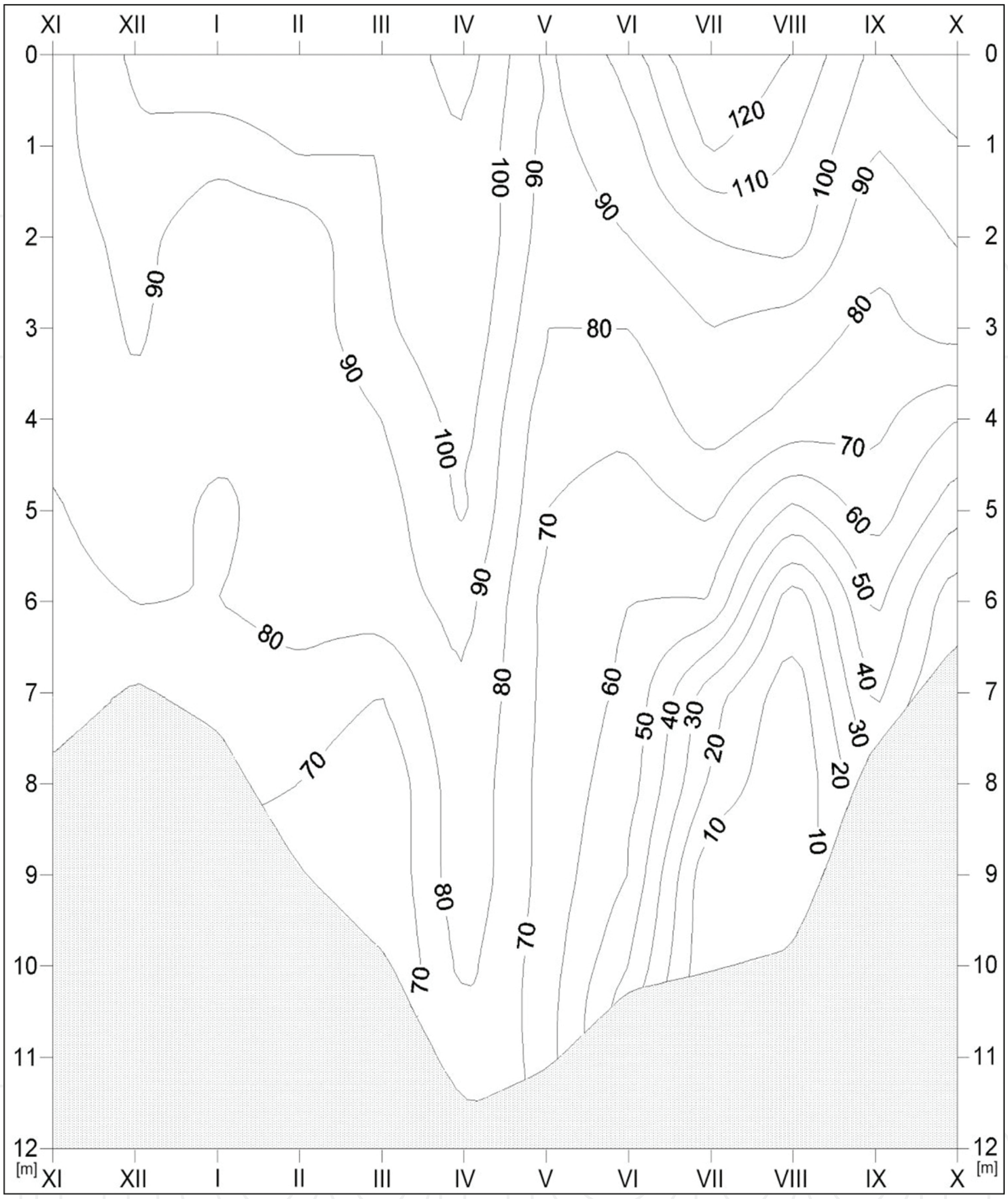

Figure 5. Oxygen saturation (in %) of the Turawa reservoir in the hydrological year 2004—vertical profile: 50°44′10.28″N, 18°05′30.22″E.

Due to increase of nutrients in limnic waters in summer, the oxygen saturation profiles are highly modified. In the Turawa reservoir, epilimnion water was oversaturated with oxygen (from 104 to 164%) because of intensive growth of phytoplankton which produces oxygen in the process. In hypolimnion, phytoplankton growth is limited and oxygen is consumed by decaying organic matter which results in drop of oxygen content. The oxygen deficit (saturation smaller than 60%) occurred from June to September. In July and August, the bottom layer of up to 6–7-m thick was completely depleted of oxygen. In fact, every year the oxygen saturation conditions of water in the Turawa reservoir were getting worse in summer period due to intensification of eutrophication processes. This is very unwanted process since oxygen deficiency is detrimental for the river fauna. With respect to oxygen content, water in the reservoir was classified to purity class III [6].

5. Conductance of water in the reservoir

Surface waters show large differences in water-specific conductance: from as low as 1μS cm^{-1} to 3000 μS cm^{-1}. Surface water conductance is strongly influenced by discharged wastewater, mainly industrial wastewater whose specific conductance can be as high as 10,000 μS cm^{-1}.

The concentration of mineral substances dissolved in water, which are responsible for water conductance, changes with time. The changes are caused by primary production, which diminishes the content of salts in water and also by the transfer of biogenic substances from bottom sediments to water which increases conductance. In the period 2004–2006, the monthly average specific conductance of water in the Turawa reservoir changed from 285 to 425 μS cm^{-1} (**Figure 6**). In the whole period studied, the lowest measured specific conductance was 272 while the highest was 495 μS cm^{-1} (average 339 μS cm^{-1}).

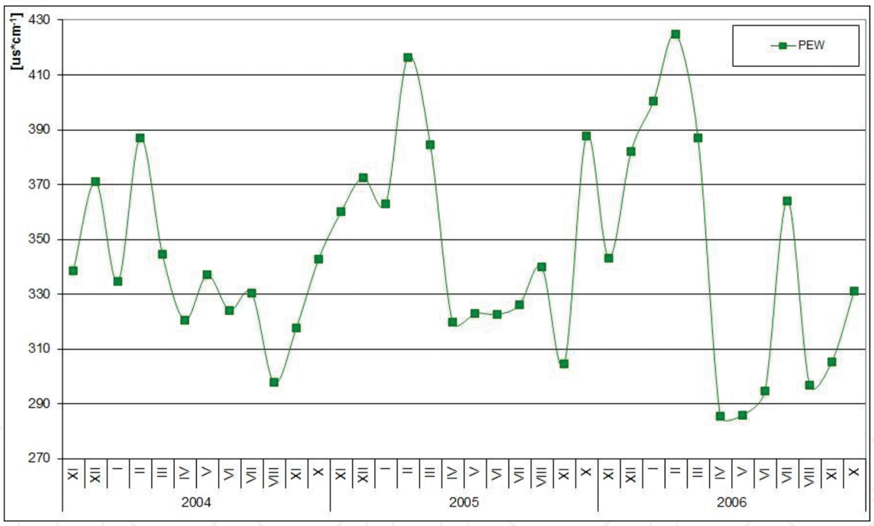

Figure 6. Changes in the average monthly specific conductance of the Turawa reservoir in the hydrological years 2004–2006.

In the season of snow melting (January and February), the conductance was the highest due to transfer to surface waters of inorganic compounds formed in the process of decay of organic matter present at the bottom and also due to runoff from spatial sources. The lowest specific conductance was measured in spring-summer season—most probably this resulted from maximum water level in the reservoir at that time. Statistically significant dependence (R^2 = 0.37) was found between the reservoir water level and conductance—the higher water level the lower the specific conductance. According to the regulations in force at that time, water in the Turawa reservoir was classified to purity class I with respect to that parameter in all measuring periods, in the hydrological years 2004–2006.

6. Water hardness

Water hardness is generally defined as the content of divalent cations, mainly calcium and magnesium in water. Hardness is divided into three categories: total hardness, temporary or bicarbonate hardness, and permanent or non-bicarbonate hardness. The total hardness or the total content of calcium and magnesium ions, generally expressed as mg $CaCO_3$ dm^{-3}, is most often used in the classification of surface water. Depending on geological characteristics of the catchment, it changes in a wide range, from several mg $CaCO_3$ dm^{-3} to several hundred mg $CaCO_3$ dm^{-3}. High hardness can be generally disadvantageous if water is to be used in household and industry. On the other hand, very low (smaller than 30 mg $CaCO_3$ dm^{-3}) hardness can be harmful for humans.

In the studied period, the monthly average total hardness in the surface water of the Turawa reservoir ranged from 106 to 191 mg $CaCO_3$ dm^{-3}. The lowest measured value of the total hardness was 95 mg $CaCO_3$ dm^{-3} while the highest was 210 mg $CaCO_3$ dm^{-3}; the monthly average hardness was 141 mg $CaCO_3$ dm^{-3} (**Figure 7**).

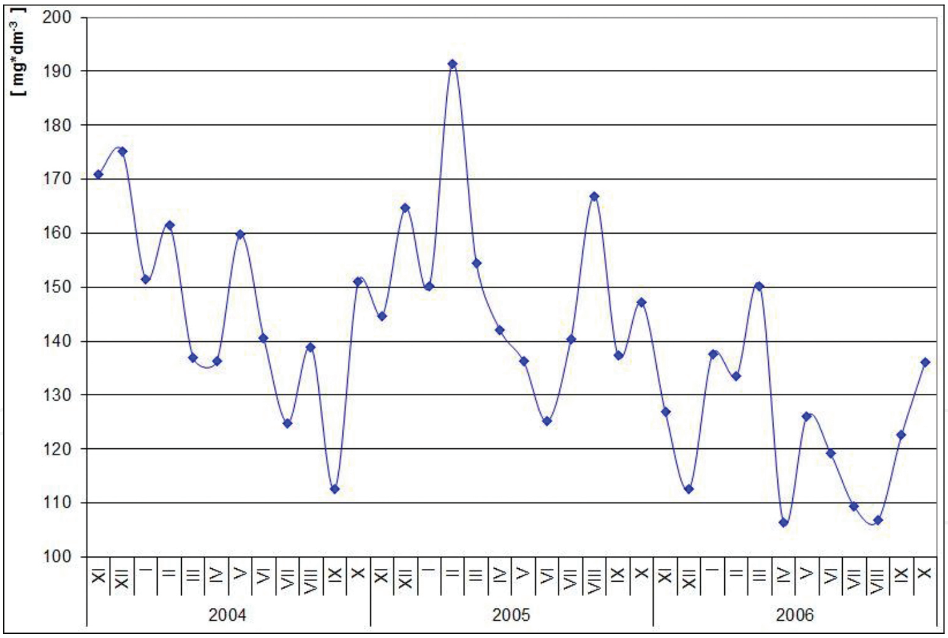

Figure 7. Changes in the average monthly total water hardness of the Turawa reservoir in the hydrological years 2004–2006.

In the studied period, the difference in the total hardness was relatively small. The water could be classified as soft or medium hard. Since the total hardness is determined by the concentration of calcium and magnesium, the changes of the monthly average concentrations of these ions were also measured. They are shown in **Figures 8** and **9**, respectively.

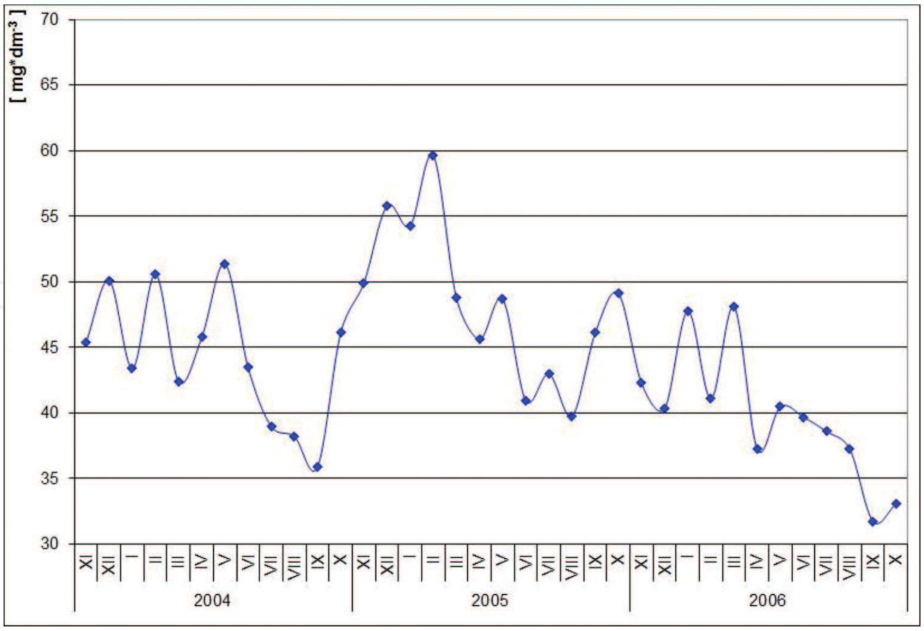

Figure 8. Changes in the average monthly calcium concentration in the waters of the Turawa reservoir in the hydrological years 2004–2006.

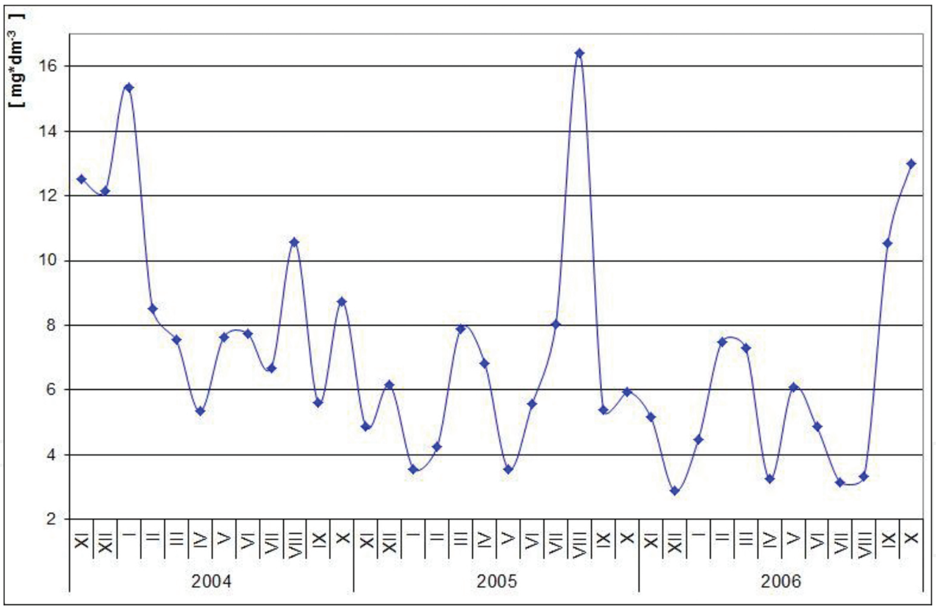

Figure 9. Changes in the average monthly magnesium concentration in the waters of the Turawa reservoir in the hydrological years 2004–2006.

Seasonal changes of calcium content were much higher than those of magnesium, which can be related to difference in solubility. The calcium content in non-polluted natural waters is generally four times higher than magnesium content. In the Turawa reservoir, it was about six times higher. The total hardness of water in the reservoir was the highest in winter, most probably due to mineralization of dead organic remains at that period.

7. Salinity changes

Water salinity is generally defined as the total content of the salts dissolved in water. In the case of storage reservoirs, usually the contents of chlorides, sulphates, potassium and sodium ions are determined in water. High salinity can be harmful to the environment and it should be monitored.

7.1. Chlorides and sulphates

The occurrence of chloride ions is common in the environment, including water. Their content in natural non-polluted water ranges from trace level to several hundred mg dm^{-3}. They are also present in vegetation and in animals. The presence of chlorides in water is responsible for the increased rate of corrosion. Chlorides are also harmful to fresh water vegetation [7].

In the hydrological years 2004–2006, the monthly average concentration of chlorides in the reservoir was in the range from 13.88 to 53.00 mg dm^{-3} (**Figure 10**). The concentration distribution was characterized by relatively low dispersion. The highest concentrations were found in early spring during snow cover melting. In winter, snow from roads was discharged into the neighbourhood of the reservoir and in the valley of the Mała Panew river. Generally, snow from the roads contains increased amounts of chlorides used in winter road maintenance. Chlorides with water from snow melting could reach the reservoir.

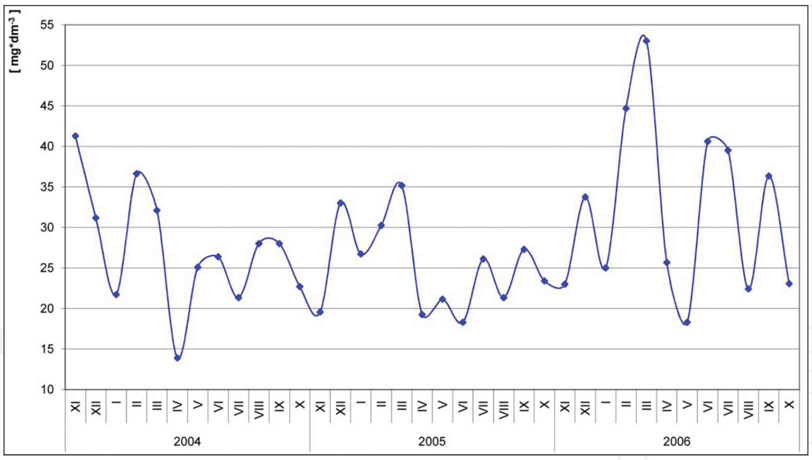

Figure 10. Changes in the average monthly chloride concentrations in the waters of the Turawa reservoir in the hydrological years 2004–2006.

The sulphates occur in natural waters in a wide range of concentrations. They are present at especially high concentrations, even up to 6000 mg dm^{-3}, in mine waters. The Turawa reservoir is surrounded by coniferous forests which assimilate larger amounts of SO_2 than deciduous forests. Sulphur in needle trees is in the form of sulphate ions, which can be leached out from fallen needles. However, anthropogenic factors had the most critical influence on the content of sulphates in the reservoir water. In the period studied, the average monthly concentration

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of sulphates in the reservoir water ranged from 28.9 to 76.7 mg dm^{-3} (**Figure 11**); the average for all the studied period was 52.2 mg dm^{-3}.

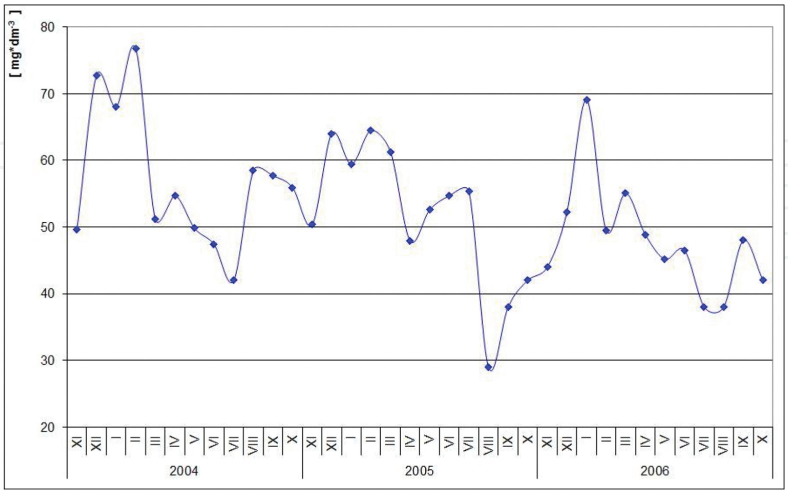

Figure 11. Changes in the average monthly sulphate concentrations in the waters of the Turawa reservoir in the hydrological years 2004–2006 (own elaboration).

The highest sulphate concentrations were found in winter due to decay of organic matter rich in sulphur compounds. In summer time, sulphate concentration dropped because living organisms were taking in sulphates and because, in anaerobic conditions in the benthic layer, they were reduced to hydrogen sulphide.

7.2. Sodium and potassium

The presence of sodium and potassium in natural waters is related to weathering of igneous rock and their leaching from sedimentary rock [8, 9]. Sodium salts are present in nearly all natural waters at the concentrations from several to 30 mg dm^{-3}. Similar to chlorides, sodium ions can come from rock salt and also from sea aerosols. There are also several anthropogenic sources of sodium, mainly wastewater from soda producing and processing industry, and from dye industry.

Potassium is usually present in natural waters in small quantity, generally at the level of several mg dm^{-3}. Strongly polluted industrial effluents and runoff water from fertilized arable land contain much higher concentration of potassium. Also in the leachate from municipal solid waste sites, potassium can be found at considerable concentrations.

In the Turawa reservoir, the average concentrations of Na^+ and K^+ ions were 12.4 and 4.5 mg dm^{-3}, respectively. In the period studied, the monthly average concentrations of sodium and potassium were in the range of 7.3–17.0 and 3.5–6.6 mg dm^{-3} (**Figures 12** and **13**), respectively. Fluctuations of Na^+ concentrations can be related to water level in the reservoir—the highest were in autumn-winter season when the water level was the lowest while the lowest were measured in spring during maximum filling of the reservoir. Seasonal changes of potassium concentration are not so distinct.

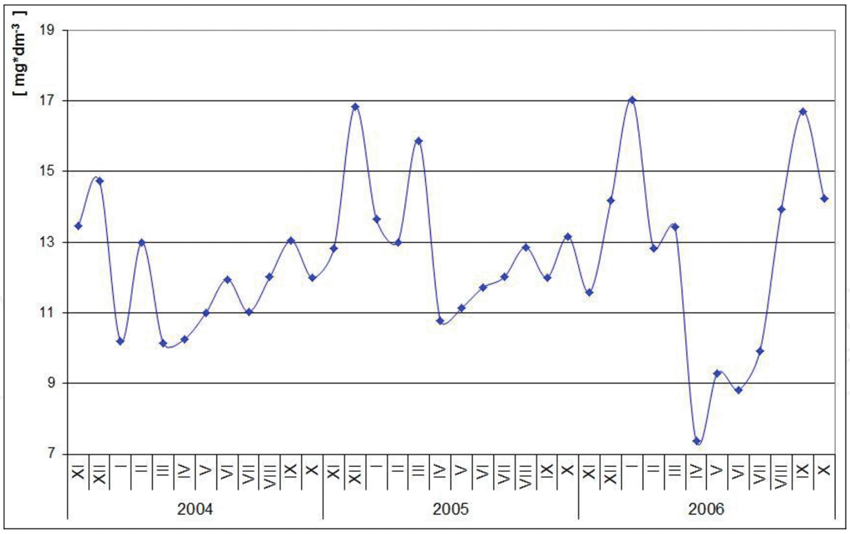

Figure 12. Changes in the average monthly sodium concentration in the waters of the Turawa reservoir in the hydrological years 2004–2006.

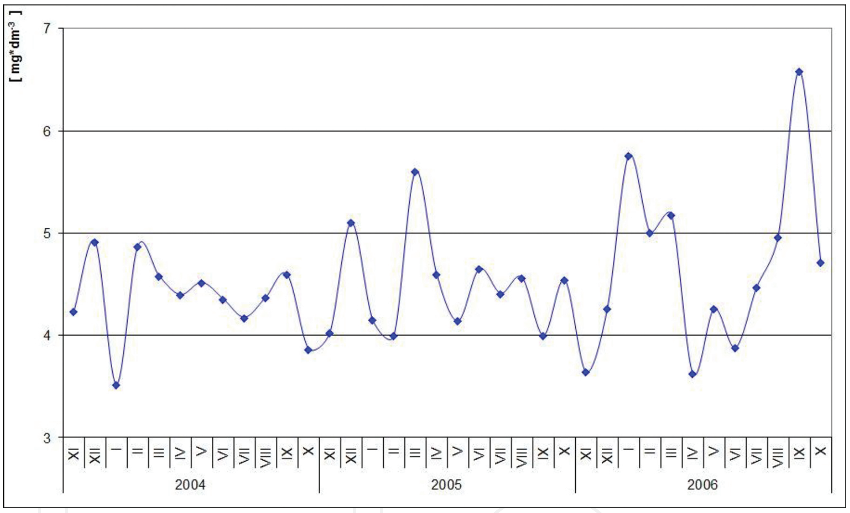

Figure 13. Changes in the average monthly potassium concentration in the waters of the Turawa reservoir in the hydrological years 2004–2006.

8. Concentration changes of organic substances

8.1. Classes of organic compounds

Surface waters can contain a wide spectrum of organic compounds belonging to different classes. The most important are carbohydrates, proteins, amino acids, esters, fats, organic acids, surfactants, soaps, ketones, alcohols, hydrocarbons, phenols, and also humic and fulvic substances. Most organic substances are of natural origin. Many are produced by animals and vegetation. They are also formed in the process of decay of dead remains of animal and vegetation. However, presently many organics found in surface waters come from anthropogenic sources. Except from humic substances, natural origin substances undergo biodegradation to simple inorganic compounds. Their presence is responsible for the deterioration of water smell and taste and can be harmful for living organisms. The presence of many anthropogenic compounds in surface water can disturb biological balance and make self-purification difficult [10].

Different human activities can really be a source of a large group of organic water pollutants. Chlorobenzenes are widely used in industry, in organic synthesis, and also as fungicides and insecticides. Some chlorophenols have fungicide and herbicide properties and some are used in producing other chemicals. Dioxins (polychlorodibenzodioxins and polychlorodibenzofurans), which are dangerous chemicals, are not produced on purpose, but they are contaminants of some chemical products. They are also formed in combustion of organic matter. Ethylenediaminetetraacetic acid is applied in steam generators to avoid precipitation of metals, in nuclear industry for surface treatment (decontamination), and so on. Glycols are used as hydraulic fluids and antifreeze agents. Polycyclic aromatic hydrocarbons are formed during forest fires, coal burning, and so on. Benzene, toluene, ethylbenzene and xylenes (BTEX) and aliphatic-chlorinated hydrocarbons are utilized as solvents. Volatile thiols can be present in the wastewater of petroleum industry. Anthropogenic phthalates are as common as natural chloride and sodium ions and presently can be found nearly everywhere; they are found in paints, inks, lacquers and solid organic polymers. Styrene can be found in plastics, synthetic rubber, copolymers; vinyl chloride is a residual monomer in polyvinyl chloride (PVC). Volatile organochlorinated compounds (VOX), mainly trihalomethanes (water chlorination), ethylene and ethane derivatives (solvents) can easily enter the environment. Some VOXs are produced by algae biomass in the process of chlorination. Pesticides include organochlorinated compounds (DDT, lindane, deldrin, etc.), organo-phosphorous compounds (parathion, malathion, etc.), sulphonates, carbamates and chlorophenoxy acetic acids. Phenols are formed in decomposition of vegetable products, can be present in industrial cellulose-containing wastewater, and were used as wood preservatives (pentachlorophenol). Sources of polychlorinated biphenyls (PCBs), pollutants widespread in the environment, are industrial wastes and leakage from transformers. PCBs undergo bioaccumulation easily. Being produced and applied or used in the production of other chemicals, organic compounds can enter the environment, including the surface water whereby they can be harmful in many ways.

8.2. Basic organic pollution parameters

Organic compounds differ greatly in physico-chemical properties and in threat to living organisms so they should be determined as groups or individual compounds. This could be and is costly and also labour- and time-consuming activity, and therefore as the first step of the determination of organic pollution, the total organic pollution parameters are used. The most typical and delivering important information on water quality are biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD). The former is a measure of content in water of organic matter that can be decomposed biologically, while the latter shows the amount of organic matter which can be oxidized by strong oxidizer as potassium permanganate (COD_{Mn}) or potassium chromate (COD_{Cr}), respectively.

The basic water quality indicators mentioned above were monitored for the Turawa reservoir. In hydrological years 2004–2006, the monthly average BOD_5 for the whole studied period was 5.2 mg O_2 dm^{-3}; it was changing in a wide range from 0.6 to 16.7 mg O_2 dm^{-3} (**Figure 14**). The annual average BOD_5 increased from 3.6 mg O_2 dm^{-3} in 2004 to 8.6 mg O_2 dm^{-3} in 2006. Occasionally, very high concentrations were found. In the period from June to September 2006, the maximum BOD_5 values exceeded 40 mg O_2 dm^{-3}.

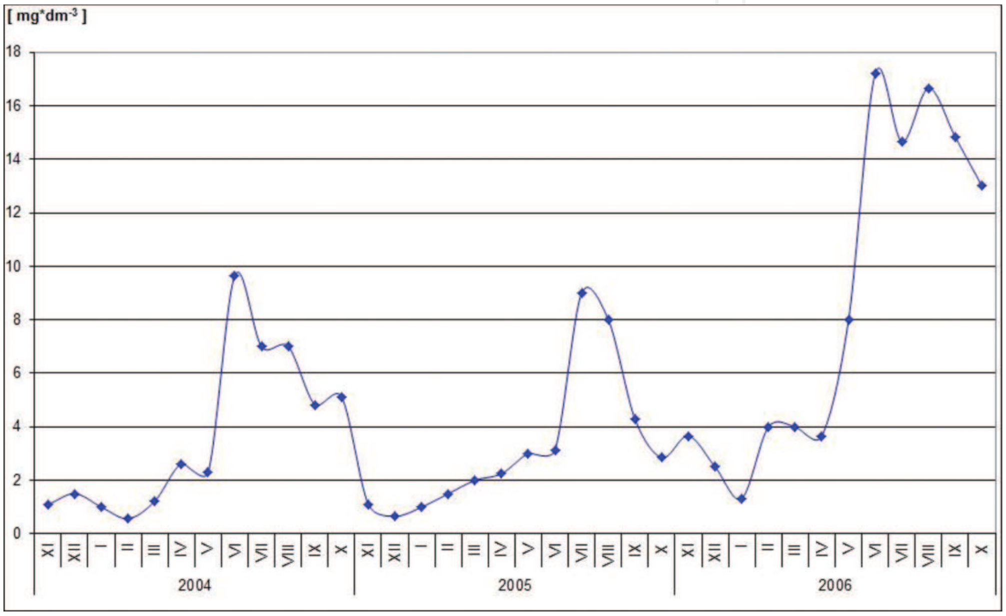

Figure 14. Changes in the average monthly BOD_5 concentration in the waters of the Turawa reservoir in the hydrological years 2004–2006.

In the above-measuring period, the monthly average COD_{Mn} parameter was 9.2 mg O_2 dm^{-3} and changed from 5.2 to 9.2 mg O_2 dm^{-3} (**Figure 15**). Occasionally, very high values of COD_{Mn} were measured, for example, from September to October 2006 the maximum COD_{Mn} values exceeded 25 mg O_2 dm^{-3}.

Both BOD_5 and COD_{Mn} values were season dependent; in winter were the lowest while in summer the highest (**Figures 14** and **15**) due to intensive eutrophication and resulting growth of algae and green algae during hot season. These organisms emit considerable amounts of organic compounds in metabolic processes and during decaying.

If water contains neither toxic substances nor organic matter resistant to biodegradation, the good correlation between BOD_5 and COD_{Mn} can be expected. For the water of the Turawa reservoir, correlation coefficient was 0.79.

In October 2006, a series of other pollution parameters were determined. They included total organic carbon (TOC), and indicators of industrial pollution such as free cyanides, phenolic index, anionic surfactants, mineral oils and polycyclic aromatic hydrocarbons. Fortunately, the

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indicators of industrial pollution were found quite low. This shows that the water in the Turawa reservoir was polluted mainly with organic matter of natural origin, which is caused by increasing eutrophication.

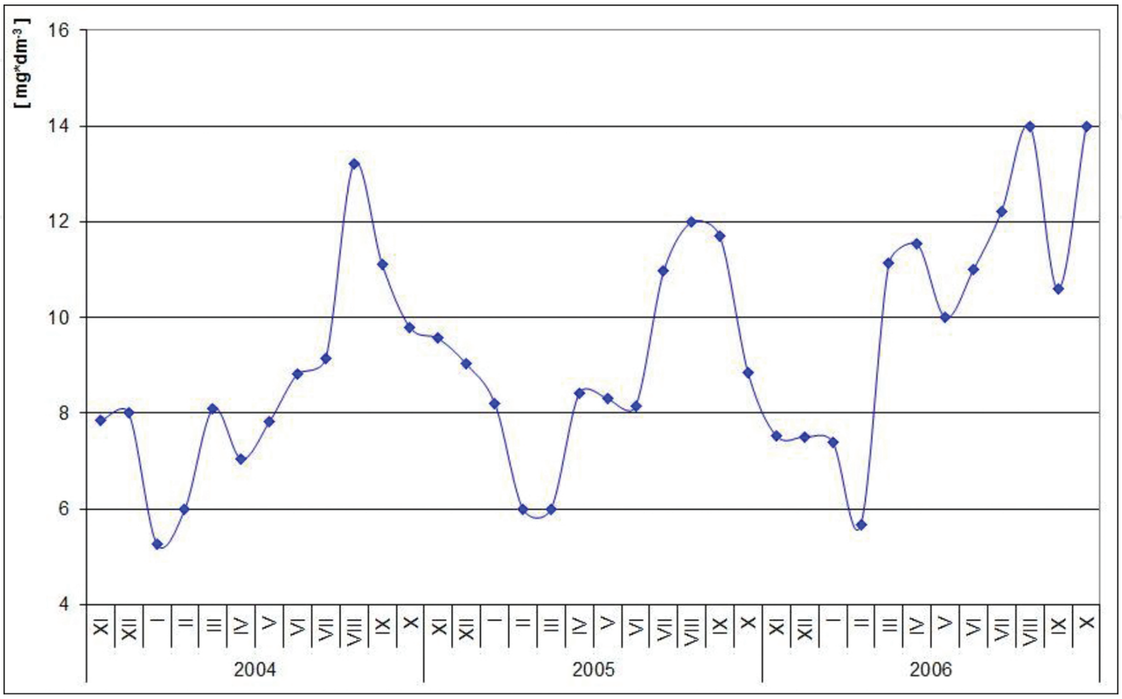

Figure 15. Changes in the average monthly COD_{Mn} concentration in the waters of the Turawa reservoir in the hydrological years 2004–2006.

9. Eutrophication processes

Eutrophication is a system response to the addition of nutrients, mainly phosphates, resulting in the 'bloom' or great increase of phytoplankton in a water body. Oversupply of nutrients, inducing explosive growth of phytoplankton and algae, results in the consumption of oxygen when these species die. The oxygen depletion level may lead to fish kills and a number of other effects reducing biodiversity. Generally, low oxygen content has many negative consequences [11, 12].

The eutrophication of the Turawa reservoir was mainly of anthropogenic origin. Nutrients were delivered by inflowing rivers, mostly the Mała Panew river; they come mainly from municipal wastewater, from arable land and forests surrounding the reservoir, and from tourist resorts. Considerable participation in eutrophication had nutrients released from bottom sediments gathering in the reservoir for tens of years. In 2004–2006, intensive release of phosphates from bottom sediments was observed during spring periods caused by water mixing. Phosphates in the form of compounds with iron or with aluminium were also released during summertime due to anaerobic conditions in the benthic layer. The intensive eutrophication in summer is favoured by hydrological and meteorological conditions such as small stream flow of inflowing rivers, low water level and high water temperature.

10. Content of heavy metals

There is no widely agreed criterion-based definition of heavy metals. Quantitative criteria used to define heavy metals included density, atomic mass and atomic number. Often applied density criteria range from above 3.5 g cm^{-3} to above 7 g cm^{-3}. In aquatic environment, heavy metals occur as micro-pollutants. Their natural sources include rock weathering, volcano eruptions, sea aerosols, forest fires and geological processes. Most important anthropological sources are transport, power industry, chemical industry, solid waste sites, fertilizers, flue gases, and so on. Heavy metals are stable pollutants and once introduced into a given environment can remain there for a long time [9].

In aquatic environment, heavy metals can be in the form of ions and dissolved complexes, and bonded to inorganic suspended matter and also to dead remains of vegetation and animals. Heavy metals are toxic species, even at rather low concentrations, and toxicity is strongly dependent on the metal. Their presence can influence the bloom of green algae.

In 2004–2006, the quarterly measurements of such heavy metals as manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), zinc (Zn), lead (Pb) and cadmium (Cd) in the water of the Turawa reservoir were conducted. They included the following: 12 measuring series were performed, 130 determinations of each metal in each series. The measurements were made for different reservoir filling to achieve the most reliable results. The program of sampling must have been precisely planned since heavy metals undergo multiple processes of desorption and adsorption during turbulent movement of water. The main source of heavy metals in the reservoir was the Mała Panew river. In the catchment of this river, zinc and lead ores were mined for about 100 years in the sixteenth/seventeenth century. At the end of the eighteenth century, mining and metallurgy of heavy metals were developed in the area again. Mines and numerous processing plants were discharging polluted industrial effluents into the Mała Panew river and its tributaries resulting in heavy pollution of river water and bottom sediments in which heavy metals accumulate resulting in steady increase in concentration. The heavy metals accumulated in sediments in the past can re-enter the liquid phase of the river water. Both forms of the pollutants, that is, dissolved in water and bonded to sediments, can be transported to the Turawa reservoir. In the years studied, there were 46 point sources discharging the pollutants to the Mała Panew river, 36 (26 industrial) of which were situated in the catchment of the reservoir. Due to the tendency to accumulate, the heavy metals were present at high concentrations in the sediments deposited in the reservoir, for example, the permissible level for cadmium was exceeded 10 times and for lead and zinc seven times. The heavy metals present in sediments can be reintroduced into the liquid phase during water rippling and flow which enhance the fluctuation of water level and hence uncovering the reservoir bottom.

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10.1. Manganese (Mn)

The occurrence of manganese in surface water is quite common. It is leached out of rocks and soil. According to some researchers, the concentration of 6 μg dm^{-3} is taken as a background for river water. The main anthropogenic sources include Mn metallurgy and burning coal and petrol. In small amounts, manganese is needed and present in vegetation and animals. It plays the role of catalyst in biochemical processes.

In the Turawa reservoir, the average content of manganese was 0.0590 mg dm^{-3} and changed from below detection limit to 0.2043 mg dm^{-3}. The highest concentration was determined in winter due to advantageous conditions of leaching from subsoil. In summer, the content dropped due to adsorption on suspended matter.

According to surface water classification, the reservoir water, with respect to Mn content, was classified most often as the second class of purity, and occasionally as the first class in summer and as the third in winter.

10.2. Iron (Fe)

Iron is quite common in the lithosphere; its content is about 5%. It is present in mineral waters due to the process of leaching out of rocks and soil. Considerable amounts are released into surface water with wastewater from the plants processing iron and with mine water. Its typical concentration in surface water is on the level of several mg dm^{-3}. Depending on the content of organic matter, oxygen, carbon dioxide, microorganism activity and pH, iron can be present in water in a dissolved form, as colloids and suspended mater. Some iron compounds can be assimilated by aquatic organisms.

In the water of the Turawa reservoir, the average iron concentration was 0.1338 mg dm^{-3} and changed in the range of 0.009–0.4145 mg dm^{-3}. According to surface water classification in the years the studies were conducted, the reservoir water with respect to Fe content was classified as purity class I in summertime, as class II in autumn-winter period when, at the low level of water and the increased bottom exposure, iron compounds are leached out of sediments.

10.3. Cobalt (Co)

Cobalt concentration in surface water is quite small, most often single to several μg dm^{-3}. The main anthropogenic sources are industrial waste and coal burning. In non-polluted surface waters, its typical concentration is 0.05 μg dm^{-3} while the natural average content is about 0.02 μg dm^{-3}. Cobalt undergoes the process of bioaccumulation in phytoplankton and accumulates in bottom sediments.

In the water of the Turawa reservoir, the average cobalt concentration was about 12.0 μg dm^{-3} and ranged from below detection limits to 62.6 μg dm^{-3}.

10.4. Nickel (Ni)

In water, nickel can be present in dissolved form as a two-valent cation, or in the complexes, most often as cyanide complex or in undissolved form as cyanide, sulphide, carbonate or hydroxide. In pure waters, its concentration is about 5 μg dm^{-3}, while in strongly industrialized areas, surface waters can contain up to about 0.020 mg dm^{-3}. Considerable amounts of nickel are emitted during combustion of diesel fuel [13].

In the water of the Turawa reservoir, the average cobalt concentration was about 6 μg dm^{-3} and ranged from below detection limits to 16.5 μg dm^{-3}. According to surface water classification in force in the years studied, the reservoir water with respect to Ni content was classified as purity class I. Only occasionally, the limiting concentration for class I was slightly exceeded.

10.5. Copper (Cu)

Copper is quite common in the earth crust; its content is about 0.02%. In water, it is in the form of quite mobile complexes with humic and fulvic acids. Copper compounds are easily bonded to sediments. Copper is present in mineral waters due to the process of leaching out of rocks and soil. The natural concentration of copper in surface waters is about 0.002 mg dm^{-3}. The main anthropogenic sources of copper are metallurgy, copper-processing factories, corrosion of products made out of this metal and its numerous alloys. Copper compounds are used as biocides to kill blooming algae [14].

In the water of the Turawa reservoir, copper concentration ranged from non-detectable to 0.0202 mg dm^{-3} with an average of 0.0111 mg dm^{-3}. According to surface water classification in force in the years studied, the reservoir water with respect to Cu content was classified as purity class I. The highest concentration was found in summertime during intensive water blooming since algae are capable to accumulate heavy metals, including copper. Algae were able to assimilate up to 90% of copper present in the reservoir.

10.6. Zinc (Zn)

Zinc in the earth is present in the form of minerals though its occurrence is not common. Small amounts of zinc can be found in water due to leaching from soil. However, the main sources of zinc in surface water are effluents of zinc smelters, zinc processing factories, chemical industry and coal burning. Pipe corrosion can also be a source of zinc in water, especially in drinking water. Polluted waters contain zinc at a concentration of 0.005–0.015 mg dm^{-3}.

In the water of the Turawa reservoir, the average zinc concentration was about 35.4 μg dm^{-3} and ranged from below detection limits to 169 μg dm^{-3}. According to surface water classification obligatory in the years studied, the reservoir water with respect to Zn content was classified as purity class I.

10.7. Lead (Pb)

Despite common occurrence in the earth crust, lead content in natural waters is low. However, due to common pollution of surface waters with lead, it is rather difficult to assess its natural content. Lead is present at 0.003 mg dm^{-3} in non-polluted waters. The main anthropogenic sources of lead are chemical industry, mining and ore-processing industry. In industrial areas whereby non-ferrous metal smelters are present, atmospheric precipitation can be a source of lead in surface waters [14].

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In the water of the Turawa reservoir, the average lead concentration was 0.0116 mg dm^{-3}; it changed from non-detectable to 0.412 mg dm^{-3}. According to surface water classification obligatory in the years studied, the reservoir water with respect to Pb content was most often classified as purity class III and occasionally as class IV. The high concentration resulted from the fact the Mała Panew river delivering 87% water to the reservoir was strongly polluted with heavy metals, including lead. Most lead in water bodies collects in bottom sediments where from it can later move back to water.

10.8. Cadmium (Cd)

Cadmium, in the free form, is not present in the earth crust, but occurs in ores of other heavy metals, mainly zinc. It is very toxic and accumulates in living organisms. It is one of the most dangerous substances on the earth. The main sources of surface water pollution with cadmium are industrial effluents from cadmium mining and metallurgy and corrosion of galvanic covers. It is also present in some phosphate fertilizers. In non-polluted waters, it is present at 0.02 μg dm^{-3}. Cadmium remains in water for relatively long time, then precipitates as carbonate and undergoes adsorption on suspended matter and sediments. In the process of bonding to sediments, bacteria participate converting cadmium compounds to CdS [14].

In the water of the Turawa reservoir, the average Cd concentration was 0.0025 mg dm^{-3}; it changed from non-detectable level to 0.0164 mg dm^{-3}. According to surface water classification, the reservoir water with respect to Cd content was most often classified as purity class IV and occasionally as class V. The high concentration in the water of the reservoir resulted from the process of chemical denudation of this element in the catchment area of the Mała Panew river. Cadmium present at high concentration in bottom sediment did not re-enter water layer since it is sparingly soluble in neutral and alkaline solution. Leaching of cadmium took place only at the lower level of water (in winter) when some part of the reservoir bottom is uncovered. The additional reason of cadmium pollution is runoff from arable land whereby phosphate fertilizers and dolomite fertilizers produced out of waste of lead and zinc mining and metallurgy are applied. Lower concentration of cadmium was observed during intensive blooming of algae which can absorb up to 80% of cadmium in the reservoir. It was found out that vegetation and animals take in cadmium at the rate proportional to its content.

11. Conclusions

Conducting the studies on the conditioning and effects of physico-chemical properties of the water in the Turawa reservoir in the hydrological years 2004–2006 confirmed the hypothesis that its ecological status was deteriorating due to strong agricultural and industrial anthropopressure.

The changes of physico-chemical properties of the reservoir were determined by the quality of inflowing river water, mainly the Mała Panew river, and inflow of pollutants from localities and resorts without the appropriate sewage systems. Moreover, the biological and chemical processes proceeding in the reservoir resulted in the changes of physico-chemical properties of water.

According to the guidelines of monitoring programme of lakes, the Turawa reservoir is characterized by moderate susceptibility for anthropopressure according to morphometric, hydrological and basin characteristics. However, the water of the reservoir could have been classified as the third class of purity, that is, as water strongly polluted.

According to the qualitative classification of surface water, the reservoir was classified as unsatisfying (class IV) or bad (class V) with respect to oxygen-related parameters (BOD_5 and COD_{Mn},), total organic carbon, microbiological parameters and also to the concentration of heavy metals such as lead and cadmium.

In 2004–2006, due to strong eutrophication the following physico-chemical parameters of water worsened: colour, odour, oxygen saturation, transparency, pH, BOD_5 and COD_{Mn}. Positive tendency of decreasing water hardness and concentrations of calcium, magnesium and sulphates took place.

One of the largest threats of ecological status of the reservoir was water eutrophication which threatens ecosystem operation. The most important threats were oxygen deficit in deep areas of the reservoir which is dangerous for aerobic organisms, oxygen oversaturation of epilimnion, decrease in water transparency, pH increase, accumulation of organic matter, reservoir overgrowing, deterioration of taste and smell, and release of phosphorous compounds in anaerobic conditions. Progressing degradation of aquatic environment decreases the usable value of water, lowers the aesthetics of the environment and management of all the water bodies.

Deteriorating ecological status of the Turawa reservoir was required to take immediate comprehensive measures to prevent it from total degradation. Remedial propositions were as follows:

- Proper management of solid wastes and wastewater and building sewage system around water body.
- Reduction of runoff of nutrients out of the catchment to the reservoir (building of wastewater treatment plant).
- Increase in year average water table elevation.
- Reducing fluctuations of water table level.
- Decreasing the content of phosphorous and heavy metals in bottom sediments.
- Removal of bottom sediments.

After 10 years, the physico-chemical parameters are being measured again to assess the results of remedial actions.

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References

[1] Tsakovski S, Kudlak B, Simeonov V, Wolska L, Namiesnik J. Ecotoxicity and chemical sediment data classification by the use of self-organising maps. Analytica Chimica Acta. 2009; 631: 142–152.

[2] Simeonov V, Wolska L, Kuczyńska A, Gurwin J, Tsakovski S, Protasowicki M, Namieśnik J. Sediment-quality assessment by intelligent data analysis. TrAC Trends in Analytical Chemistry. 2007; 26: 323–331.

[3] Wang S, Huang Z, WuYu-S, Winterfeld PH, Zerpa LE. A semi-analytical correlation of thermal-hydraulic-mechanical behavior of fractures and its application to modeling reservoir scale cold water injection problems in enhanced geothermal reservoirs. Geothermics. 2016; 64: 81–95.

[4] Bocaniov SA, Ullmann Ch, Rinke K, Lamb G, Boehrer B. Internal waves and mixing in a stratified reservoir: Insights from three-dimensional modeling. Limnologica – Ecology and Management of Inland Waters. 2014; 49: 52–67.

[5] Jorgensen SE; Loffler H; Rast W; Straskraba M; Evaluating Lake and Reservoir Water Quality. Chapter 3, Developments in Water Science. 2005; 54. Elsevier Science, ISBN: 9780080535340.

[6] Hudson JJ, Vandergucht DM. Spatial and temporal patterns in physical properties and dissolved oxygen in Lake Diefenbaker, a large reservoir on the Canadian Prairies. Journal of Great Lakes Research. 2015; 41: 22–33.

[7] Bernhardt-Römermann M, Kirchner M, Kudernatsch T, Jakobi G, Fischer A. Changed vegetation composition in coniferous forests near to motorways in Southern Edition Germany: The effects of traffic-born pollution. Environmental Pollution. 2006; 143: 572–581.

[8] Bartarya SK. Hydrochemistry and rock weathering in a sub-tropical Lesser Himalayan river basin in Kumaun, India. Journal of Hydrology. 1993; 146: 149–174.

[9] Gaillardet J, Viers J, Dupré B. Trace Elements in River Waters, Treatise on Geochemistry. 2003; 5: 225–272

[10] Gerbersdorf SU, Cimatoribus C, Class H, Engesser KH, Helbich S, Hollert H, Lange C, Kranert M, Metzger J, Nowak W, Seiler TB, Steger K, Steinmetz H, Wieprecht S. Anthropogenictrace compounds (ATCs) in aquatic habitats—Research needs on sources, fate, detection and toxicity to ensure timely elimination strategies and risk management. Environment International. 2015; 79: 85–105.

[11] Liu Y, Wang Y, Sheng H, Dong F, Zou R, Zhao L, Guo H, Zhu X, He B. Quantitative evaluation of lake eutrophication responses under alternative water diversion scenarios: A water quality modeling based statistical analysis approach. Science of The Total Environment. 2014; 468–469: 219–227.

[12] Munyati C. A spatial analysis of eutrophication in dam reservoir water on the Molopo River at Mafikeng, South Africa. Sustainability of Water Quality and Ecology. 2015; 6: 31–39.

[13] Mirabi A, Shokuhi RA, Nourani S. Application of modified magnetic nanoparticles as a sorbent for preconcentration and determination of nickel ions in food and environmental water samples. TrAC Trends in Analytical Chemistry.2015; 74: 146–151.

[14] Bilal M, Kazi TG, Afridi HI, Arain MB, Baig JA, Khan M, Khan N. Application of conventional and modified cloud point extraction for simultaneous enrichment of cadmium, lead and copper in lake water and fish muscles. Journal of Industrial and Engineering Chemistry. 2016; 40: 137–144.