

SURFACE WATER QUALITY ASSESSMENT IN THE PIRIN NATIONAL PARK, BULGARIA

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Abstract

The protected area of Pirin National Park as a UNESCO heritage site is very important not only because of the exceptional biological diversity but also because of the water resources in a big quantity and excellent quality used for drinking water supply of all adjacent cities and villages, as well as for all human activities in this region. At the same time the Park is a very attractive touristic destination for people from all over the world both in winter and summer periods. From this point of view the protection of the surface water bodies at the catchment area of the Park against the pollution is a task of a great importance. The main objective of the study is to assess the quality of the main river and lake water bodies in the Pirin National Park. Data from the local monitoring on the water chemistry (electro- conductivity, temperature, pH, Biological Oxygen Demand, Chemical Oxygen Demand, as well as the concentration of Dissolved Oxygen, Suspended Particle Material, Dissolved compounds, $N-NH_4^+$, $N-NO_3^-$, $P-PO_4^{3-}$, Fe and Mn) for the period 2004-2013 have been treated statistically. During the periods of high and low water level in 2014 a visit to 28 river and lake water bodies at the territory of the Park has been organised for observation, sampling for water chemistry, analysing and measuring of some parameters in the field. After processing and discussing the results obtained a recommendation is given to the point and diffuse sources of water pollution on how to protect the quality of the surface water in the Park.

Key words: diffuse and point sources, glacial lakes, pollution, rivers, water chemistry

1. INTRODUCTION

The quality of surface water bodies strongly depends on the environmental conditions at their catchment areas. The Pirin Mountain is located in Southwestern Bulgaria and the larger part of this mountain (26 413.8 ha) is included in the Pirin National Park, established in 1962. Since 1983, the park has been protected as a UNESCO Heritage Site. The park includes one of the oldest reserves in Bulgaria– Bayuvi Dupki – Dzhindzhiritsa. The area was granted this status in 1934 so as to protect the endangered black and white fir (*Pinum peuce*) and the habitats of many other plants and animals. In 1977, this reserve was included by UNESCO on its list of reserves as part of the “Man and Biosphere” program, as was the park’s Yulen Reserve, in 1994.

The main objective of the study is to assess the quality of the main river and lake water bodies in the Pirin National Park. The follow tasks have been taken into account:

- 1) Characteristic of the main biotic and abiotic environmental conditions at the catchment area of water resources in the Pirin National Park;
- 2) Determination of the point and diffuse sources of pollution of the surface water in the park;
- 3) Statistical treatment of available monitoring data for the chemistry of the surface water bodies in the park;
- 4) Visiting, sampling and analysing the taken samples from the main river and lake water bodies in the park both in the field and laboratory;
- 5) Assessment the quality of surface water resources in the park by comparing the results obtained with the standards of the European Legislation.

2. MATERIALS AND METHODS

2.1. Site description

The annual temperature varies within the ranges of about 9-10°C in the low mountain zone, 5-7°C in the middle mountain zone and within 2-3°C in the highest parts of the mountain (Bansko – 9.3°C, Popina laka– 7.1°C, Vihren chalet – 3.5°C). The coldest month is January with an average temperature of about – 2°C to – 5°C. The hottest month is July - the average monthly maximum temperatures in July and August are almost equal and are about 20°C at the altitude of 1600 m and about 15°C at the altitude of 2000 m. The annual rainfalls vary in the range of 600-700 mm in the low mountain to 1000-1200 mm in the highest zones. Greater portion of the rainfalls in the winter is of snow as in the altitude up to 1000 m the solid falls are about 70- 90% of the total rainfall quantity and in the highest zones they reach 100% of the total rainfall quantity. The average thickness of the snow cover varies in wide ranges. The maximum snow thickness is:- In lower parts (with an altitude 700-800 m) is during January – 10-13 cm; - For the altitudes of 1000-1800 m is in February – about 40-60 cm; - Above 1800 m it is at the end of March-beginning of April - about 140-160 cm (Vihren –190 cm). In some winters the maximum snow cover could reach 250-350 cm.

The highest point of the Park is on top of the mountain Vihren (2.914 m), situated in the middle part of the Park, between the valleys of the Struma River (western side) and the Mesta River (eastern side). The lowest point is situated at the entrance of the park at Bansko (950 m.)

The geological fundament of the mountain belongs to the Rhodopian Super group – metamorphic rocks. Biotite schists and gneisses, amphibolites, quartzites and marbles are the predominant rocks (about 25% of the territory). Paleozoic granitoids cover small areas around the borders of the park. Late Cretaceous granitoids build up two clearly distinguishable structures: the North-Pirin and the Bezbog plutons. The first one consists of medium-grained granites and the second one consists almost entirely of porphyric biotite granites to leucogranites. The Central-Pirin pluton covers almost the whole southern part of the park and consists of granites. Altogether granitoids cover about 55% of the territory of the park. Proluvial Quaternary fans occur only in the lowest part of the park, close to the town of Bansko. Glacial deposits are concentrated in the cirques and the glacial valleys. They consist of gravel and blocks of granite, gneiss and marble. The tectonic structure of the Pirin Mountain is mainly a result of Precambrian, Hercynian, Alpine and Neotectonic movements. The Alpine structure of the mountain is dominated by faults and tectonic magma phenomena. A period of planation in the Early Miocene leads to the formation of the main denudation surface (peneplain). The Neo-tectonic movements lead to the destruction of the peneplain and complete development of all faulting zones that divide the Pirin horst from the surrounding grabens. The relief of Pirin National Park is notable for its alpine character – strong segmentation, steep slopes, high ridges and deep river valleys.

The development of the karst in the Pirin National Park is connected with the distribution of the Pre-Cambrian marbles on the territory of the mountain. The intensive neo-tectonic movements and the chemical composition of the marbles, as well as their jointing and the substantial rain-falls sum have predetermined the development of a large number of predominantly vertical caves. According to the regional division of the caves in Bulgaria (Popov, 1976) the territory of the Park within the so called Vihren-Sinanitsa cave region (402), which covers an area of 57.2 km² and could be divided into two subregions– Vihren and Sinanitsa. As a result of the long-term expeditions carried out by the Bulgarian cave divers a total of 113 precipices and precipice caves have been studied, mapped and classified till now in this region.

The Park occupies 1.89% of the Struma river watershed and 7.25% of the Mesta watershed. Rivers and river systems- on the territory of Pirin National Park 10 tributaries of Struma river and 10 tributaries of Mesta river occur and their springs are within the territory of the Park.

There are 164 lakes within this park. They are located between 2100 and 2500 meters of altitude, in the spring areas of Bunderitsa, Demianitsa, Begovitsa, Vlahinska, Tufcha, Sandanska Bistritsa, and Pirinska Bistritsa rivers, and 138 of them have permanent water surface. They are provisionally divided in 17 lake groups. The total area of the water surface in the conditions of average water levels is 2085 km². This area forms 0.51% of the Park territory. The areas of Popovi and Banderishki lakes

are the largest ones. Popovo lake is the largest (124 000 m²) and the deepest one (29,5 m) from the group of Popovi lakes.

The results from the survey show that for Pirin National Park the average annual flow is 355.6 million m³ of water, 188.5 million m³ of them go towards Struma River and 167.1 million m³ flow into Mesta river. Among the rivers, which flow into Struma the one with the greatest flow is Sandaska Bistritza River and among these ones, which flow into Mesta– it is Bjala reka River (East). With the largest in specific flow among the tributaries of Struma River is Mozgovitza River and among the tributaries of Mesta– it is Disilitza River. The flow from the park represents 40.5 % of the flow of Pirin Mountain, as the area of the Park is scarcely 17.9 % of the territory of the mountain. In comparison to the territory of the country the area of the Park is scarcely 0.36% but it gives 2.07 % of the flow of the rivers in Bulgaria. The flow per unit of the Park area is 2.3 times greater than the average flow of Pirin Mountain and 5.6 times greater than this one from the territory of the country.

Mountain brown forest soils (Humnic, Eutric and Disric Cambisols) are distributed in the middle mountain zone of beech and coniferous forests (800- 1800 m in altitude). *Mountain dark coloured forest soils* (Umbric Cambisols) are the relation to the mountain meadow soils over the upper border of the forest and the pine- scrub formations. The soil parent materials usually are granites carbonates free with high fertility. *Mountain- meadow (humus- siliceous) soils (Rankers)* are distributed almost entirely in the alpine part of the high mountain zone (over 2500 m) where they could be found often in a complex with rock and scree. In the sub alpine sub zone (up to 2500 m in altitude) they are in a complex with mountain forest dark colored soils. High- mountain grasslands are developed over these soils. The granite rock is the main soil parent material. Of the main importance for the development of *Humus- calcareous soils (Rendzinas)* are the presence of hard calcareous rocks and the products of the weathering. Mainly Pinus nigra, Pinus helderichii, Pinus mugo and Juniperus communis alpina grow over these soils.

The plant communities established could be classified into several main groups: Communities around water basins; Shrub communities in the sub-alpine zone; Herbaceous and grass communities– forest meadows, sub-alpine and alpine pastures; Forest plant communities; Communities on rock habitats and Secondary plant communities– result of anthropogenic activity. The ecosystems depending on the presence of water are of azonal character. They could be found in all zones. The most typical of them are the hygrophite and hydrophyte communities in the sub-alpine and alpine belts of the Park.

It could be concluded that all environmental, cultural and socio- economic characteristics of the Pirin National Park catchment area should be taken into account during the assessment procedure of the quality of river and lake water bodies. Although the park is a protected well forested area with a water flow 5.6 times greater than the average one from the territory of Bulgaria, the human activity is well represented including water supply facilities, forest road network, roads of other organizations, practicing of various specific types of sports and all related equipment, tourism, agricultural development etc. From this point of view the study on the impact of the activity and conditions mentioned above on the surface water quality in the park is very important in order to protect the water resources for the future generations.

2.2. Monitoring data collection

The information about the water resources use from the Pirin National Park territory has been obtained from the last Management Plan of the park (2004), Management Plans for Mesta (2010) and Struma (2010) rivers, archived data in the Direction of the park as well as in the adjacent municipalities.

Monitoring data on the water chemistry for the period 2001-2002 have been taken from the last Management Plan of the park (2004). It was recommended in this plan to organise a local monitoring on the quality of the main surface water bodies. As a result there has been a monitoring project on the water chemistry in the Park since 2004. Monitoring data for analysed parameters for the period 2004-2013 have been given by the Direction of the park. During this time the following parameters were measured 2 or 3 times a year: electro- conductivity, temperature, pH, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), as well as the concentration of Dissolved Oxygen, Suspended Particle Material (SPM), Dissolved particles (DP), N-NH₄⁺, N-NO₃⁻, P-PO₄³⁻, Fe and Mn.

All data of this local monitoring have been treated statistically, calculating the average, minimum and maximum values for each water body studied and for each parameter measured during the period 2004- 2013, as well as for all river and lake water bodies for each parameter mentioned above in separate records.

Point and diffuse sources of pollution of the surface water in the Pirin National Park have been listed as a result of personal observation during the visit to the park territory in September 2014, discussion with the representatives of the Direction of the park, owners of the buildings and facilities, and actualisation of the information from the last Management Plan of the park, Mesta and Struma rivers.

2.3. Sampling points

During the visit to the Pirin National Park from 25 May to 15 June 2014 (high water level) and from 9 to 14 September 2014 (low water level) water samples from 14 river and 14 lake water bodies have been sampled in 3 different bottles- one for analysing the concentration of dissolved Oxygen, the second for Biological Oxygen Demand and the third for all other chemical parameters. The quality of water has been assessed for the follow river and lake water bodies:

Rivers: Banderitsa river after the hut Vihren (Fig. 1, left), Banderitsa river on the border of the park, Demyanitsa river on the border of the park, Sinanishka river on the border of the park, Vlahinska river on the border of the park, Demyanitsa river after the hut Demyanitsa, Desilitsa river on the border of the park, Pleshka river on the border of the park, Bezbojka river on the border of the park, Bela river in the Betalovoto, Retije river on the border of the park, Kamenitsa river on the border of the park, Bzeznishka river on the border of the park, Jelezina river on the border of the park and Mozgovitsa river on the border of the park.

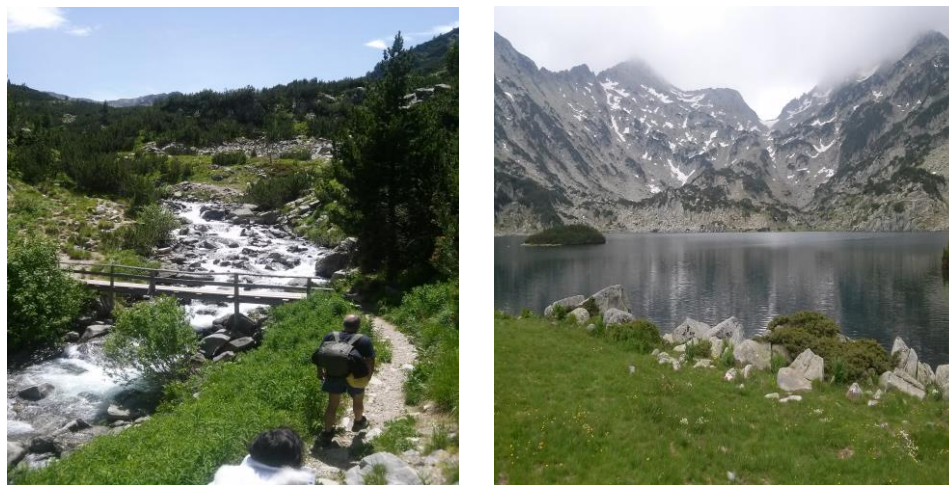
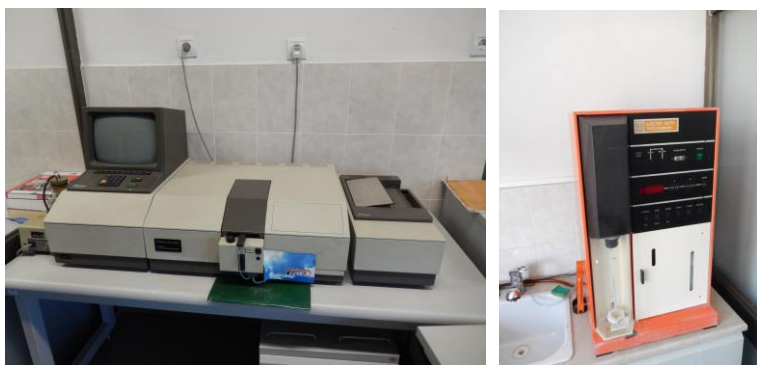


Fig. 1 Sampling points for Banderishka river (left) and Popovo lake (right)

Lakes: Ribno Banderishko lake, Dalgo lake, Jabeshko lake, Okoto lake, Vasilashko Tevno lake, Gorno Vasilashko lake, Dolno Vasilashko lake, Popovo lake (Fig. 1, right), Ribno lake, Bezbojko lake, Valyavishko lake, Gorno and Dolno Kremensko lakes, as well as Tevno Malokamenishko lake.



Fig. 2. Fixing the dissolved Oxygen (left) in the water from lake with eutrophication (right)



Individual water samples of surface water have been collected after measuring the **temperature, pH and conductivity** on separate aliquots of the unfiltered sample the same day of sampling in the field by Jon meter “Combo” of the “Hanna Instruments”.

2.4. Methods for chemical analyses

All samples have been filtrated through 0.45 μm cellulose filter using membrane filtrating system in order to remove any solid materials and to stabilize them for the subsequent analyses, and stored in the refrigerator at 1-4 $^{\circ}\text{C}$ until analyses. The chemical composition of the water samples has been determined as follow: **$N\text{-NH}_4^+$ and $N\text{-NO}_3^-$** -using Kyeldal automatic distillation and titration by 0,1 n HCl (Nitrogen Analyser Tekator, Sweden), **SO_4^{2-}** - by UV/VIS Spectrometry “Lambda 5, Perkin Elmer” after precipitation by BaCl_2 in the presence of 1 N HCl and gelatine to stabilize the colloidal solution of BaSO_4 , and measuring the absorbance at 490 nm wavelength, **CT** by means of precipitation with AgNO_3 , **$P\text{-PO}_4^{3-}$** by UV/VIS spectrometry ‘Lambda 5, Perkin Elmer after the treatment of 25 cm^3 portions of water samples with 15 cm^3 of combined reagent (2,5 M H_2SO_4 , potassium antimony tartrate $[\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 0,5\text{H}_2\text{O}]$, ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{26} \cdot 4\text{H}_2\text{O}]$ and ascorbic acid) in volumetric flask of 100 cm^3 and measurement the absorbance of developed colour at the 880 nm wavelength. **The concentration of dissolved O_2** has been determined by Winkler method (Ignatova, 1998), fixing the samples in the field by adding 2 cm^3 of MnSO_4 (40%) and 2 cm^3 of KOH (40%) (Fig.2). After transporting the samples to the laboratory 10 cm^3 of H_2SO_4 (1:4) have been added, as well as 2 cm^3 of KI (10%), samples have been put it in the dark for 10-15 minutes, titrated with 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ until the colour became light yellow, and after adding 0.5 cm^3 $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ as indicator, titrated with the same solution until the liquid was colourless. **The content of suspended particle material** (C_{SPM} , $\text{mg} \cdot \text{dm}^{-3}$) has been determined as follow: bottles with cellulose filter (0.45 μm) has been heated in oven at 102 $^{\circ}\text{C}$ for half an hour, after 10 minutes of cooling down measured. Filters have been used for filtering 200 cm^3 of the sample, put back in the same bottles, heated in oven at 102 $^{\circ}\text{C}$ for half an hour and after cooling down, measured again. For measuring **the biological oxygen demand (BOD)**

the small bottle with the second water sample has been stored in a dark at 20 °C for 5 days and after that the concentration of dissolved O₂ has been measured again by the same method of Vinkler.

3. RESULTS AND DISCUSSION

3.1. Information about the water resources use from the Pirin National Park territory

Drinking and households water supply

A number of catchments installations for drinking and households water supply for local facilities—chalets, vacation homes, etc., are developed on the territory of the Park. The waters are used mainly on the territory of the Park. The irreversible water loss of the drinking and households water represents 8-12% of the waters caught. The used waters flow back in the river currents following surface and underground way and they don't represent considerable disturbance of the flow. Waters from the territory of the Park are also used for supplying small villages situated out of the Park. The caught waters flow back in the river network out of the Park territory. At present there is no sufficiently detailed survey of all the catchment installations with their characteristics, but if the small number of the population on the close proximity to the Park (less than 100 000 persons) is taken into account it could be evaluated that the annual volume of the drinking and households water doesn't exceed 2 million m³ which represents 0.56% of the surface flow from the territory of the Park and the irreversible loss is respectively about 0.06% of the flow, formed on the Park territory (Fig. 3).

Hydro-energy: On the territory of Pirin National Park there are facilities of the Sandanska Bistritza cascade. 8 catchments with built up water quantity of 6.48 m³.s⁻¹ are developed. The caught waters in an annual cross-section represent usually about 20% of the built up water quantity or 1.3 m³.s⁻¹. The average perennial volume of the caught waters could be estimated of about 41 million m³ or of about 50% of Sandanska Bistritza river flow, which is formed on the Park territory. After processing of these waters in the water electric power station "Liljanovo" they enter into a derivation where together with another caught waters they proceed to the "Sandansky" electric power station and after the processing they flow again into the Sandanska Bistritza river.

Water Sources for Water Supply: The cold and clear Pirin waters (springs and rivers) provide the water supply for the chalets, hotels, and rest houses within the park and its contact zone. Spring waters are captured in the following areas: Kalugeritsa locality to supply Razlog city, the springs of Tsigansko Kladenche, Pelevi Izvori, Usina, and drainage catchments and drilling wells to supply Bansko city, a spring near Bunderitsa river to supply Akademika rest house and Bunderitsa chalet, the springs of Kruntia, Studenia Chuchur, Shiroka Poliana, to supply Obidim and Mesta villages, the springs of Perlesh and Shulai to supply Dobrinishte village, springs near Melnishka river below Stefanov peak to supply Sugarevo village and Melnik, springs at Sinanishka river in Mandrata locality, Studenata Voda spring at Razkolska river and Chernata Voda spring at Vlahina river to supply Kresna, local catchments to supply the chalets of Yavorov, Pirin, Vihren, river catchments at Struzhka river and Valevitsa river to supply Simitli, Alexova river catchment to supply Predela locality and Razlog city.

Table 1. List of point sources of water pollution in the Pirin National Park

№	Point source	Period of impact	EC, max	EC, mean daily
1	Treatment plant Banderishka polyana	Winter	641	504
2	Treatment plant Shiligarnika	Winter	556	310
3	Treatment plant Platoto	Winter	400	240
4	Tourist zone Vihren	Summer	180	85
5	Hotel "Secret"	Winter	80	80

6	Hotel "Tofana"	Winter	70	70
7	Hut "Bezboj"	Year	120	60
8	Shelter "Tevno lake"	Summer	100	60
9	Hut "Sinanitsa"	Summer	60	48
10	Hut "Banderitsa"	Summer	140	45
11	Tourist zone Yavorov	Summer	97	45
12	Hut "Demyanitsa"	Summer	220	40
13	Restorant "Banderitsa"	Year	140	40
14	Hut "Begovitsa"	Year	100	30
15	Shelter "Spano pole"	Year	40	15
16	Hut "Pirin"	Year	80	10

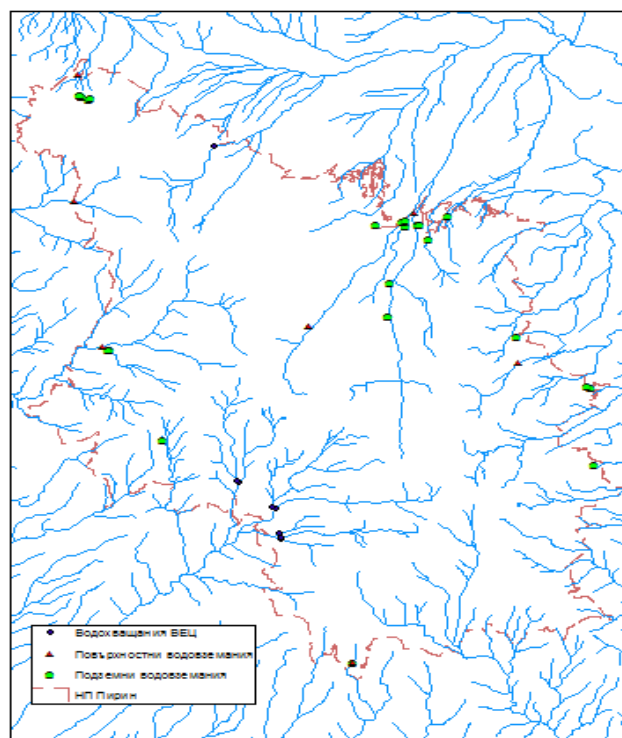


Fig. 3. Use of water resources in the Pirin National Park for power plants (Blue), Water extraction from stream water bodies (red) and from underground water bodies (green) (After L. Markovski, G. Georgiev, 2014)

3.2. Point and diffuse sources of water pollution

The point sources of pollution are the huts, restaurants, tourist zones, shelters and treatment plants. These are listed in the Table 1. Some of point sources of water pollution are situated far away from the treatment plants for waste water, connection with canalization systems is not possible and there are septic pits but the majority of these collecting equipment does not function as it is need for protecting the water resources like septic pits of the huts Demyanitsa, Vihren, Bezbojka etc.

Sewerag: The establishment of a centralized sewerage is obstructed by the fact that the sites are scattered and far from each other. There are two forms of treating the waste waters from the sites:

- Grouping the sites into a common sewerage (in a given area)– ViK Rest House, Ribarnika villa, DZI Rest House, Izvorite Hotel, PSS Rest House (Vihren PR);
- All the rest buildings within the park are serviced by septic pits, which are in poor condition.

Waste water: The water flow (spring, surface and waste) from the territory of the Pirin National Park and its adjacent territories flows into the rivers Mesta and Struma. Until the year 1990 the main polluters by organic matter of the valley have been the industrial factories in the region of the town of Razlog. Since 1990 because of the closing of the Plant (for ecological reasons) and the reduction of the production of the Cellulose and Paper Plant the character of the pollution of the river valley changed.

Of the total of 16952 m³ daily sewage water, 10419 m³ daily or 61.5% of the total volume of the waste water flows into Mesta River without treatment. The treatment effect of the existing treatment facilities is low and only the municipality of Razlog has a treatment station for the households sewage water. A project is elaborated in the phase of the preliminary studies for the building of a town water treatment plant in Bansko Municipality.

The problem of treatment of the sewage water is not tackled in Gotse Delchev Municipality.

Thanks to the influx down the stream of the crystal clean water of the tributaries and the great self purifying potential of the river, the waters of Mesta River close to the border are very slightly polluted and leave the Bulgarian territory almost clean.

Of the total of 13 603 m³ daily sewage water, 11 404 m³ daily or 83,8% of the total volume of the waste water flows into Struma River without treatment (this concerns only the territories adjacent to Pirin park). The pollution of the river waters by organic matter of household origin is high because the household waste water of the region flow into the river without treatment, which is an indirect sign of the presence of bacterial pollution. At present there is a waste water treatment plant for the town of Pernik and projects for town water treatment station in the Simitli and Sandanski Municipalities.

In the boundaries of Pirin National Park the territories designated for grazing are 9300.8 ha, of which 5029.1 ha belong to the agricultural and 4271.7 ha areas belong to the forested areas. All the grazing regions are located in territories of traditional regime of agriculture use, and have been divided in 5 park regions.

The carrying capacity of pastures was calculated on the basis of the pastures' "productiveness", the daily need of nutritive substance (in fodder units) and the continuity of the grazing period.

In the period 1995 – 2001 the number of animals, which have grazed in pastures of the park's different regions has been smaller than the pastures' capacity, which is an indicator that the park's pastures have not been overloaded. Certain, but not excessive overloading of the pasture territories has been registered only in Vihren Park Region in the period 1995 - 1998, where more animals have grazed than the pasture capacity allows. In the following years in the region of Kamenitsa, which has the biggest capacity, the actual number of grazing animals has been 3-4 times smaller than the pasture's capacity allows.

The number of cows, sheep and horses in the Park for the period of 2009-2013 could be seen in the Table 2. Only the number of cows has been increased during this period. The impact of all animals in the park is estimated to be equal to 59256 Population Equivalent in 2013 which is more than in 2009 by about 3394 units.

Table 2. Impact of animals on the catchment area in the Pirin National park for the period 2009-2013
(After Markovski, Georgiev, 2014)

Parameter	Unit	2009	2010	2011	2012	2013
Cows	Number caws	2529	2554	2682	2818	2872
Horses	Number horsts	94	87	67	62	45
Sheeps	Number sheeps	3514	3125	3228	2693	3007
Area allowed for pasture	ha.	6677,8	6538,7	6795,8	6711,7	6963,1
Area allowed for pasture	dka.	66778	65387	67958	67117	69631
Total impact	EC /day	55862	54807	57107	57400	59256
Impact of N (90 days)	kg/dka/year	0,828	0,830	0,832	0,847	0,842
Impact of P (90 days)	kg/dka/year	0,136	0,136	0,136	0,139	0,138
Impact of BDO (90 days)	kg/dka/year	4,517	4,526	4,538	4,618	4,595
Impact of N (120 days)	kg/dka/year	1,104	1,106	1,109	1,129	1,123
Impact of P (120 days)	kg/dka/year	0,181	0,181	0,182	0,185	0,184
Impact of BDO (120 days)	kg/dka/year	6,023	6,035	6,050	6,158	6,127

3.3. Monitoring data treatment

The monitoring data for the surface water chemistry of the main water bodies during the low and high water level in 2001-2002 represent a very good quality of the studied water bodies. All obtained values corresponded to the standards of the highest quality of surface water. Non organic Nitrogen and Phosphorus were practically absent at this period, except ammoniac nitrogen in the spring season for a small part of the rivers and lakes. In addition the values of Biological and Chemical Oxygen Demand have shown that any organic loading of the both river and lake water bodies on the park territory was missing.

The monitoring data for the next period 2004- 2013 have represented some problems with pH values (moderate state) for the river Banderista both before and after Banderishka polyana and the concentration of N-NH_4^+ after this local source of pollution (Table 3). The 'before' and 'after' the table stands for the sampling point before the points of pollution and after the points of pollution. The quality of water of Sandanska Bistritsa was moderate after the Biological Oxygen Demand as well as Demyanishka river after the N-NO_3^- . For all other river water bodies the concentrations of all measured parameters correspond to the norm for "excellent" and "good" water quality.

Table 3. Statistical treatment of monitoring data for the chemistry of all studied river and lake water bodies, 2004- 2013.

	pH	O ₂ , mg.dm ⁻³	O ₂ , %	Electr., μs.cm ⁻¹	BOD ₅	COD	DC	SPM	N-NH ₄ ⁺	N-NO ₃ ⁻	P-PO ₄ ³⁻
<i>Rivers</i>									mg.dm ⁻³		
Mean 2004-2013	7,75	9,13	98	50,85	0,97	1,81	45	14	0,051	0,124	0,061
min 2004-2013	6,80	6,01	11	17,50	0,26	0,01	6	2	0,003	0,002	0,004
max 2004-2013	9,44	12,90	139	215,00	3,75	7,06	184	36	0,782	0,879	0,755
Excellent	6,5- 8,5	10,5- 8,0		650	≤ 1,0				≤ 0,04	≤ 0,2	≤ 0,01
Good	6,5- 8,5	8,0- 6,0		750	1,0- 2,5				0,04- 0,40	0,2- 0,5	0,01- 0,02
Moderate	6,5- 8,5	≤ 6,0		≥ 750	≥ 2,5				≥ 0,40	≥ 0,5	≥ 0,02
<i>Lakes</i>											
Mean 2004-2013	7,81	8,24	101	33,84	1,35	0,96	35	12	0,052	0,095	0,055
min 2004-2013	6,99	5,28	10	11,30	0,53	0,60	4	4	0,003	0,003	0,006
max 2004-2013	9,00	10,70	134	111,00	3,52	1,60	94	30	0,193	0,300	0,303
Excellent	6,5- 8,7	10,5- 8,0		650	≤ 1,0				≤ 0,03	≤ 0,2	0,007- 0,0125
Good	6,5- 8,7	8,0- 6,0		750	1,0- 2,5				0,03- 0,08	0,2- 0,5	0,0125- 0,04
Moderate	6,5- 8,7	≤ 6,0		≥ 750	≥ 2,5				≥ 0,08	≥ 0,5	≥ 0,04

Some problems could be discovered for the quality of some lakes for the same period concerning not only pH, dissolved O₂, N-NH₄⁺, but also P-PO₄³⁻. For example the waters of Okoto, Bezbojko and Ribno lakes correspond to the standards for the “moderate” water quality for N-NH₄⁺, N-NO₃⁻ and P-PO₄³⁻. (Table 3).

Taking into account the statistical data shown in the Table 3, it should be mentioned that for the majority of parameters the quality of the water in both rivers and lakes studied during the period of monitoring (2004- 2013) was “excellent” or in a couple of cases “good” but the presence of the orange colour, corresponding to the “moderate” water quality, for ammoniac nitrogen and phosphate phosphorus for both rivers and lakes is a reason to assess comparatively the quality of their water once again during the periods of high and low water level, which is the main objective of this study.

3.4. Surface water quality assessment

3.4.1. Surface water quality assessment during the period of high water level

The results of the observation, measurements in the field and chemical analyses for assessment the quality of the main river and lake water bodies during the period of high (in June 2014) and low water level (in September 2014) are presented in table 4 and 5 respectively. The values are compared to the norms and assessed under “excellent” (blue), “good” (green) and “moderate” (orange) water quality (Low for the water, 135, al.1, point 17, Standards for water quality, State Gazette N 4/2008, Regulation N H4, State Gazette N 22/5.03.2013 and changes in State Gazette N 79/23.09.2014, WFD, 2000/60). The assessment of water quality after the chemical parameters is a part of the complex ecological assessment.

The values for the parameters of water chemistry of both rivers and lakes during the period of high water level confirm that after the parameters dissolved oxygen, acidity and electroconductivity all studied water samples were in “excellent” quality. It was found that the mean concentration of N-NH_4^+ in lakes was 10 times higher ($1,45 \text{ mg.dm}^{-3}$) than in rivers with a norm for “maderate” water quality more than $0,08 \text{ mg.dm}^{-3}$. The mean concentration of N-NO_3^- for selected lakes is $0,92 \text{ mg.dm}^{-3}$, wich corresponds to the “moderate” water quality. “Excellent” water quality could be appropriated only to two lakes (Tevno Malokamenishko lake and Dolno Kremensko lake) (Table 4).

In the group of rivers the highest concentration of N-NH_4^+ has been found for Banderitsa, Desilitsa and Retije rivers. The water quality of rivers Pleshka, Bezbojka and Pirinska Bistritsa is “excellent” after the concentration of N-NO_3^- . For Desilitsa river and Dalgoto and Jabeshko Banderishki lakes the N-NO_3^- corresponds to the “moderate” water quality, and for all other water bodies the quality of water belongs to the “good” state. The load of water bodies by organic compounds expressed by the Biological Oxygen Demand is very low, remaining higher for rivers ($2,41 \text{ mg.dm}^{-3}$) than for lakes ($1,84 \text{ mg.dm}^{-3}$) (Table 4).

Table 4. Averadged water chemistry data for 28 surface water bodies “rivers” (R1, R3, R5, R14) and “lakes” (L1 и L3) during the period of high water level in the Pirin National Park, mg.dm^{-3} , May- June 2014 r.

Data	pH	Electr., $\mu\text{S.cm}^{-1}$	SPM	N-NH_4^+	N-NO_3^-	SO_4^{2-}	P-PO_4^{3-}	BOD_5	O_2
Rivers									
Mean	7,56	51,68	3,44	0,16	0,52	5,28	0,0021	2,41	9,71
Min	7,01	21,4	1,41	0,02	0,11	1,72	0,0015	1,24	8,34
Max	8,36	124,2	5,61	0,54	1,22	11,23	0,0023	5,22	11,44
Norm									
Excellent	6,5-8,5	650		$\leq 0,04$	$\leq 0,2$		$\leq 0,01$	≤ 1	10,5-8
Good	6,5-8,5	750		0,04-0,40	0,2-0,5		0,01-0,02	1- 2,5	8-6
Moderate	6,5-8,5	≥ 750		$\geq 0,40$	$\geq 0,5$		$\geq 0,02$	$\geq 2,5$	≤ 6
Lakes									
Mean	7,54	14,06	1,96	1,45	0,92	1,58	0,016	1,82	9,50
Min	6,87	4,6	0,61	0,01	0,27	0,19	0,006	0,64	8,07
Max	8,54	22,5	5,06	3,73	2,82	3,27	0,025	4,93	10,96
Norm									
Excellent	6,5-8,7	650		$\leq 0,03$	$\leq 0,2$		0,007-0,0125	≤ 1	10,5-8
Good	6,5	750		0,03-0,08	0,2-0,5		0,0125-0,04	1- 2,5	8-6
Moderate	6,5	≥ 750		$\geq 0,08$	$\geq 0,5$		$\geq 0,04$	$\geq 2,5$	≤ 6

The electroconductivity of water as an integral parameter of the water quality ranges from 21,4 to 124,2 $\mu\text{S.cm}^{-1}$ for rivers and from 4,6 to 22,5 $\mu\text{S.cm}^{-1}$ for lakes which shows an “excellent” state taking into account that the norm for the best water quality is 650 $\mu\text{S.cm}^{-1}$.

Very low values have been measured for suspended particulate materials in water bodies too. The mean concentration of this integral pollutant has been 3,44 mg.dm^{-3} for rivers and 1,96 mg.dm^{-3} for lakes respectively.

Although problems mentioned above, in general the predominant water quality for river and lake water bodies in the park is “**excellent**” or “**good**” after the parameters analysed in this study.

3.4.2. Surface water quality assessment during the period of low water level

Concerning the acidity (pH), conductivity, and the concentration of sulphates and dissolved Oxygen, the quality of surface water of both rivers and lakes is “excellent” (blue colour) for the period of low water level. The mean values of pH for rivers and lakes are very close- 8,11 pH units for rivers and 8,08 for lakes respectively. In general, the water bodies are very rich in dissolved O_2 - 8,07 mg.dm^{-3} for rivers and 9,30 mg.dm^{-3} for lakes. All studied water bodies are cold and clear visually with a very low concentration of suspended particle materials (2,66 mg.dm^{-3} for rivers and 3,51 mg.dm^{-3} for lakes as an average value). The acidifying Sulphates are represented by very low values of their concentration. The mean concentration of SO_4^{2-} in the lakes studied in September 2014 has been only 2,43 mg.dm^{-3} with a maximum value of 4,93 mg.dm^{-3} for the Dolno Vasilashko lake. Values measured for the rivers range between 2,76 mg.dm^{-3} for Banderitsa river and 18,77 mg.dm^{-3} for Vlahinska river, with an average for all rivers 7,94 mg.dm^{-3} which is much lower than the norm (Table 5).

The presence of different colours in the columns for Nitrogen and Phosphorus in 2014 confirms the tendency of increasing the concentration of N-NH_4^+ and P-PO_4^{3-} in the water of rivers and lakes mentioned in the discussion on the monitoring data for the period 2004- 2013. The average concentration of Ammoniac Nitrogen for rivers is not high (0,09 mg.dm^{-3}) with a highest value of 0,37 mg.dm^{-3} for Desilitsa river. The quality of surface water is ‘excellent’ for 8 rivers and ‘good’ for 7 of them after this parameter, but concerning the lakes, only 3 of them have a “good” quality and 7 “moderate” with concentrations between 3,9 and 0,59 mg.dm^{-3} (Table 5). All water bodies are suitable for drinking water supply, because the norm for this purpose is 0,50 mg.dm^{-3} , except the Okoto lake (0,59 mg.dm^{-3}) (Regulation N 9, 2001).

Only 6 rivers and 6 lakes should be included in the group of “excellent” water quality concerning the concentration of Nitrate Nitrogen, 4 rivers and Jabeshko lake in the group of “good” quality, 5 rivers and 3 lakes in “moderate” with a highest value of 1,2 mg.dm^{-3} for Retije river (Table 5).

The distribution of the river water bodies in accordance with the concentration of P-PO_4^{3-} could be listed as follows: the quality of water is “excellent” for 2 rivers (Desilitsa and Pleshka), “moderate” for 2 other rivers (Banderitsa and Mozgovitsa) and all other 11 rivers could be considered as a “good” quality. The mean concentration of P-PO_4^{3-} is equal to 0,01 mg.dm^{-3} for both rivers and lakes. The water of 50 % of lakes studied are in a “excellent” state and the water quality of 50 % of the lakes is “good”. During the practical work in the field for observation, sampling and measuring some parameters during the sampling in 2014, it has been found that the eutrophication was well developed in some lakes, sometimes even with small white flowers like in Dolno and Gorno Vasilashki lakes as well as Ribno (almost totally covered by algae) and Bezbojko lakes. Dolno Vasilashko lake has been used for developing the fishery without any permission and there were a lot of cows in the catchment area of Ribno and Bezbojko lakes close to water bodies.

Table 5. Averadged water chemistry data for 28 surface water bodies “rivers” (R1, R3, R5, R14) and “lakes (L1 и L3) “during the period of low water level in the Pirin National Park, mg.dm⁻³, 9-15 september 2014 r.

Data	pH	Electr., μS.cm ⁻¹	SPM	N-NH ₄ ⁺	N- NO ₃ ⁻	SO ₄ ²⁻	P-PO ₄ ³⁻	BOD ₅	O ₂
Rivers									
Mean	8,11	78	2,66	0,09	0,41	7,84	0,010	3,79	8,07
Min	7,35	14	0,11	0,01	0,01	2,76	0,001	0,06	3,73
Max	8,56	305	6,01	0,37	1,20	18,77	0,022	7,83	13,12
Norm									
Excellent	6,5-8,5	650		≤ 0,04	≤ 0,2		≤ 0,01	≤ 1	10,5-8
Good	6,5-8,5	750		0,04-0,40	0,2-0,5		0,01-0,02	1- 2,5	8-6
Moderate	6,5-8,5	≥ 750		≥ 0,40	≥ 0,5		≥ 0,02	≥ 2,5	≤ 6
Lakes									
Mean	7,77	11,46	3,51	0,20	0,36	2,33	0,019	4,26	9,20
Min	6,87	5,1	0,61	0,01	0,01	1,39	0,01	1,77	7,8
Max	8,54	18,2	6,50	0,59	1,02	4,93	0,038	12,02	16,4
Norm									
Excellent	6,5-8,7	650		≤ 0,03	≤ 0,2		0,007-0,0125	≤ 1	10,5-8
Good	6,5	750		0,03-0,08	0,2-0,5		0,0125-0,04	1- 2,5	8-6
Moderate	6,5	≥ 750		≥ 0,08	≥ 0,5		≥ 0,04	≥ 2,5	≤ 6

In addition the majority of the huts and other buildings and facilities at the territory of the park are not included in the canalization systems and they use only the septic space for collecting the waste water. This could be an explanation for the relatively high values of the Biological Oxygen Demand in both lakes and rivers. The highest values of this parameters have been measured for Dalgo Banderishko lake (12,02 mg.dm⁻³) and for Banderishka river just after the Vihren hut (7,83 mg.dm⁻³) which corresponds to the norm for “moderate” water quality. The quality of the water for the rest of rivers and lakes is moderate with an average of 4,39 mg.dm⁻³ for lake water bodies and 3,79 mg.dm⁻³ for rivers, but in accordance with the Water Framework Directive 60/2000 EC untill 2015 all water bodies should obtaine at least “good” water quality (Tables 5). At the same tame the touristic activityin the park is higher during the periods of low water level than in late spring season with high water level. From this point of view it is essential to collect information about the point and diffuse sources of surface water pollution by organic compounds, nitrogen and phosphorus.

4. CONCLUSION

- The water flow per unit of the Pirin National Park area is 2.3 times greater than the average flow of Pirin Mountain and 5.6 times greater than this one from the territory of the country. The park is extremely rich in cold and crystal clear surface water with exiting biological diversity;
- It could be evaluated that the annual volume of extracted water for the drinking and households water supply represents only 0.56% of the surface flow from the territory of the Park and the irreversible loss is respectively about 0.06 % of the flow, formed on the territory of the Pirin National Park, which doesn't represent considerable disturbance of the flow;
- In general the predominant water quality for river and lake water bodies in the park is “**excellent**” or “**good**” after the parameters analysed in this study with some exceptions for N-NH_4^+ , N-NO_3^- , Biochemical Oxygen Demand and P-PO_4^{3-} .
- Equipments for the extraction of water for drinking water supply are not protected enough and they are accessible for people and animals which does not correspond to the regulation norms;
- A small number of point sources of water pollution are grouped into a common sewerage (in a given area) and all the rest buildings and facilities within the park are serviced by septic pits, which are in poor condition;
- It is recommended to implement local treatment equipment for all point sources releasing waste water outside of the area with a common canalization system at the territory of the park based on the increasing concentration of Nitrogen and Phosphorus in the surface water;
- The impact of animals is estimated to be equal to about 60000 Population Equivalent at the areas allowed for the pasture but the improvement of the survey for respecting this status should be recommended;
- It could be strongly recommended to stop the seasonal development of the fishery in the glacial lakes above 2000 m in the Park in order to avoid the increasing of the production of the algae biomass causing eutrophication.

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