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ANALYSIS OF SURFACE WATER KEY POLLUTANTS OF THE TRIBUTARIES OF THE DANUBE RIVER IN BULGARIAN SECTION

M. Filipova, I. Zheleva, A. Lecheva, P. Rusev

Based on official data, a comparative analysis of the surface water along the rivers flowing into the Danube River in the transborder area Bulgaria–Romania is presented. The content of dissolved oxygen, nitrate nitrogen and Biological and Chemical Oxygen Demand (BOD_5 and COD) for a five year period 2009–2013 is analyzed. The aim is the dynamics of these indicators and the reasons for the current exceedances to be traced and analyzed. Measures for improving the condition of the surface runoff are also proposed.

1. Introduction

Pursuant to the operational European program for CBC Bulgaria - Romania for the period 2007–2013 [1] includes the border areas of both countries. This program creates a connection between the two countries and aims to promote and support the development of the regions situated on both banks of the Danube. We are currently discussing the continuation of this program in the new programming period year 2014–2020. So, together with Romania good results along the Danube and the Danube region could be achieved to make one of the best places to live.

An important indicator for the successful development of the region, to protect human health and the natural resources is the water quality. Water is the defining element of human existence. We cannot imagine a human activity, the

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presence of life forms and the current balance without water. Water is a renewable natural resource, a source of energy and an important factor in maintaining the ecological balance. Water is used for many different purposes: agricultural;industrial; transport and other purposes. This leads to serious pollution of the water resources and is a serious threat to the ecological balance in nature. A typical example of this exploitation and unreasonable attitude of man to the state water resources is one of the largest rivers - the Danube, in its section between Bulgaria and Romania. It is well known that wastewater from thousands of settlements, industrial sites and agricultural areas are flowing into the river. Good coordination between all Danube countries, environmental understanding between them and their joint efforts in the global European policy on the Danube will help to restore the purity of the river. Danube water catchment is very large and diverse. It supports different ecosystems (karst caves, alpine steppes and lakes, floodplain forests,delta) and various wetlands of European importance.

This paper provides an analysis of the monitoring network along the Bulgarian section and is referred to, the cities with significant contamination of surface water. For building a monitoring system Ordinance №1 of 11.04.2011 have been issued [3]. The purpose of the ordinance is to settle the terms and conditions of planning and monitoring the establishment of networks for monitoring water in all river basin districts, also to regulate tasks and activities for operation, maintenance, communications and laboratory information service. According to this regulation, the monitoring of groundwater bodies include programs for the quantitative status of surface water bodies, programs and operational control monitoring of chemical status.

2. Geographical location of the Bulgarian section of the Danube River

Fig. 1 shows the Danube River basin. It includes territories or parts of territories of many European countries – Germany, Austria, Czech Republic, Slovak Republic, Slovenia, Hungary, Croatia, Bosnia and Herzegovina, Serbia, Romania, and Bulgaria.

Particular interest to the Bulgaria–Romania border region represents the state of the Danube River. Biological research in the Bulgarian section of the Danube (399 km) shows alarming results: places for recreation around the river are weakened to the extreme limit; deterioration of water quality and it becomes dangerous to human health; overall pollution of the river with mineral substances – hydrogen carbonates, sulfates, chlorides – in recent years, growing by about 1 percent per year; nutrient pollution – nitrates, nitrites, ammonia, phosphorus,

Figure 1: The Danube River Basin

threatens water quality; biomass decreases in places; benthic fauna is completely destroyed – in the sections below major industrial centers; bacteriological load increases, particularly worrying is the increase of salmonellosis causes; outflow of household waste seriously exacerbated ecological imbalance in the region.

Responsibility for water quality in the border Bulgarian section of the Danube River, according to the Water Act, is assigned to the Danube River Basin District administrative center of Pleven. This section covers the most of territory of northern Bulgaria. The area of the region is 42 837 km^2, which is more than 38% of the territory of Bulgaria and 44% of the total population. In the Danube region there are 111 municipalities, 15 districts, 25 water companies. In the region is also the country's capital, Sofia (in Iskar sub-basin), which is the fastest developing economic center of Bulgaria. The Danube River Basin District (DRBU) includes the valleys of rivers flowing into the Danube River or crossing the western boundary of the country which are shown in Fig. 2.

- Along the Erma and Nishava – catchment area of the River Erma on Bulgarian territory is 523 km^2 and flows into the River Nishava (with a catchment area of Bulgarian territory – 331 km^2) and empties into the River Morava and then into the Danube River.

- Ogosta's valley along with the rivers in the west of Ogosta - the valley is located in the northwestern part of Bulgaria between Western Balkan, Timok, Danube and along the Iskar River. The rivers of the basin originate from the main ridge of the Balkan Mountain except Tsibritsa and Skomlya that spring from the foothills of the Balkan Mountain. A significant part of the rivers in the basin are flowing directly into the Danube – Topolovets,

Figure 2: Scheme of the river flows of the Bulgarian Danube River Basin District Management [2]

Voinishka, Vidbol, Archar, Skomlya, Lom, Tsibritsa, Ogosta, Skat (are listed in order of acquisition in the Danube river). The total area of the sub-basins is 8022 km^2, and the total annual flow is 1 254 106 m^3. Larger rivers are Lom with 202 106 m^3 annual runoff and Ogosta with 750 106 m^3 annual runoff.

- Iskar River is the longest internal river in Bulgaria with a length of 368 km and catchment area of 8646 km^2. Originates from south part of the Rila Mountain (Gyolechitsa – Cherni Iskar, Prav Iskar), south-southwest of Govedarci, Sofia and south-southwest of its highest peak Musala (Levi Iskar, Beli Iskar). It occupies part of the territory of six administrative districts: Sofia, Sofia region, Pernik, Vratsa, Pleven and Lovech with a population of about 1.6 million inhabitants. There are 25 major tributaries, some of the big ones are – Iskar (85.5 km), Stari Iskar (65.2 km), Zlatna Panega (50.3 km) and others. The larger right tributaries are the Lesnovska, Iskar and Zlatna Panega and larger left tributaries are Palakaria River, Blato and Slivnishka, Kakach, Ruchene, Gaberska.

- Vit River has length of 189 km and a catchment area of 3220 km^2. There are about 10 inflows with average lengths of 10 km. The larger inflows are the river Kamenska with length 49 km and a catchment area of 500 km^2 and the river Kalnik – with length of 41 km.

- Along the Osam – formed by the merger of the rivers Cheren and Beli

Osam near the town of Troian. Both of its major tributaries originate from the northern slopes of the Troyan Balkan, located in the Central Balkan Mountain. The length of the river is 314 km, and the area of its catchment area – 2824 km^2. Catchment area is narrow with an average width of 20 km, which is the reason for the development of a dense river network. There are not many tributaries, they are short and with small watersheds – rivers Barra, Lom, Mechka etc.

- Along the Yantra – the size of catchment area along the Yantra River is the second largest area in the Danube region, after Iskar and amounts to 7862 km^2. The river is 285 km long and originates from the peak of Hadji Dimitar, approximately 1340 m altitude, and it flows into Danube at about 18 m of altitude. There are thirty tributaries with a length of 10 km. Larger ones are: river Rositsa – 164 km long and with catchment area of 2265 km^2, River Stara reka – 92 km long with an area of 2424 km^2, Djulyunitsa River – 85 km long with an area of 892 km^2.

- Valleys of Ruse's Lom River and Dobrudja's Rivers – these basins are located in the eastern part of the Danube region. In the west bordering with the watershed to Yantra River, in the south – with watersheds to basins Yantra and Kamchia, to the east - with the watershed Dobrudja rivers flowing directly into the Black Sea and to the north - by the Danube and the eastern part of the state border with Romania. Ruse Lom River is formed by the confluence of the rivers Beli and Cherni Lom. Beli Lom River originates south of Razgrad, and Cherni Lom River – southeast of Popovo. Conditional start of the river Ruse Lom is accepted to be Beli Lom. The length of the two main tributaries of Cherni and Beli Lom before merging together is respectively 130 km and 140 km with catchment areas 1549 km^2 and 1276 km^2. Dobrudja rivers keep on the surface a certain distance from their sources, but then they lose formation in the Dobrudja area and do not form a surface tributaries to the Danube. The area of the rivers is about 9809 km^2. Larger rivers are: Suha River with length 126 km and a catchment area of 2404 km^2, river Tsaratsar with length 108 km and a catchment area 1062 km^2 and a river Kanagyol – 110 km long, with 1745 km^2 catchment area.

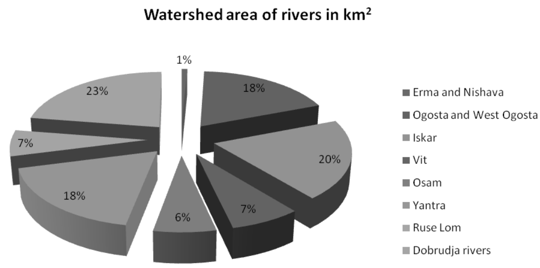

Figure 3: Watershed area of rivers in Bulgarian Danube River Basin

3. Important indicators of water quality and main pollutants [4]

3.1. Dissolved oxygen amount

Important for the life in the water bodies and the process of purification of the polluted water is dissolved oxygen (Dissolved oxygen DO). It is a key indicator of the metabolism of all aquatic organisms. Its solubility in water is low (about 10 mg/dm^3 at near atmospheric pressure), and it decreases at increasing temperature of the water. The increased concentration of dissolved substances also decreases the solubility of oxygen. The shortage and excess of oxygen are risk factors for aquatic organisms. The abundance of air in the water can lead to nitrogen narcosis, and satiety by 120–140% nitrogen already known to cause mortality in fish. The best values of dissolved oxygen for fish life are between 7–9 mg/l, and when its value falls below 3 mg/l, the values are in critical condition. Standards for dissolved oxygen, and other key indicators of water quality, are considered in accordance with Ordinance №7/1986 [4].

Concentration of dissolved oxygen in the water reflects on the balance between oxygen – consuming (breathing) and oxygen – releasing processes (e.g., photosynthesis and physical transfer of oxygen from the atmosphere into the water body). The reported values are an indicator of possible violations of these competitive processes and define the living conditions of aerobic organisms.

Concentration of dissolved oxygen in the water is directly dependent on temperature, salinity, biological activity and the rate of transfer of oxygen from the atmosphere (the main source of oxygen in an ecosystem). Organic matter from sewage effluent or dead plant material that is easily accessible to microorganisms (especially aerobic heterotrophic bacteria) has the greatest effect on the concentration of dissolved oxygen. Actual depletion depends on the load of biodegradable organic matter and the activity of microorganisms. Dissolved oxygen is the most important factor controlling the variability in nutrients and heavy metals.

Low oxygen concentrations can lead to a significant increase in the toxicity of certain pollutants (zinc, lead, copper, pentachlorophenol, cyanide, hydrogen sulfide, ammonia) and adverse effects on the efficient functioning of aquatic fauna.

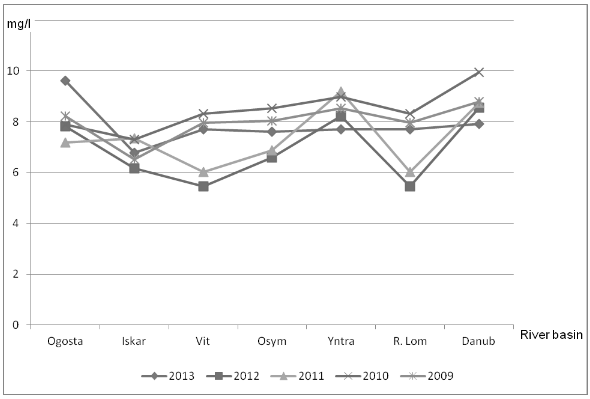

Figure 4: Amount of dissolved oxygen in river basins [5]

Fig. 4 shows the average values of dissolved oxygen in different river basins over a 5 year period 2009–2013. It can be seen that there are significant differences in the oxygen content in the different basins and years. The lowest values of dissolved oxygen were recorded in 2012, and the highest in 2010 and in 2013. In the valley of Ogosta is observed a significant increase in dissolved oxygen, along the Iskar it has lower values, while in the remaining basins the values of dissolved oxygen in 2013 are almost identical. Values lower than the average for the valleys are registered in points Novgrad of the Yantra River, Trojan of the Osam River, Roman and Gigen of the Iskar River etc.

The oxygen content in the water depends on various factors: abiotic (temperature, vertical and horizontal circulation) and biotic (development of photosynthetic organisms, putrefactive processes, etc.). The analysis of annual data showed that lower levels of dissolved oxygen are in the second and third quarter of each year. This is due to the increased biological activity, oxidative processes, and reduced vertical and horizontal mixing of waters. During winter periods, the reduction processes are weakest, leading to higher values of the oxygen.

3.2. Biological oxygen demand (BOD_5)

Another important indicator of water quality is the biological oxygen demand (BOD_5). This index serves as a measure for consuming oxygen in a specific time interval - in this case 5 days for the aerobic biochemical oxidation of organic substances contained in the test water. High concentrations of BOD_5 indicate high organic content in the water, i.e. measure of organic pollution. Fig. 5 shows the average content of BOD_5 in river basins over a 5 years period 2009–2013.

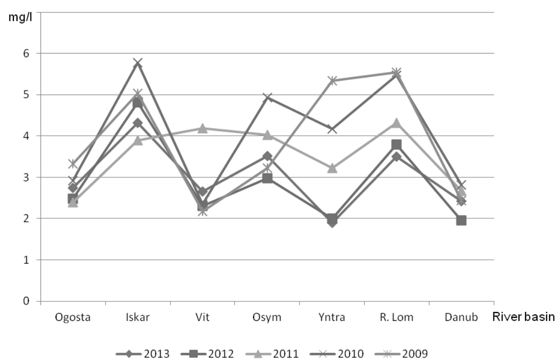

Figure 5: Biological oxygen demand (BOD_5) in the rivers [5]

It could be seen that the highest values of BOD_5 are registered in the valleys of the rivers Iskar and Ruse Lom, and lowest values in the valleys of the river Vit and Yantra. It could be seen also that in the last two years - 2012 and 2013 there was a decrease in average values, the most significant is decrement along the Yantra River. Compared to the average of the valleys, higher values were recorded in points: Novi Iskar and Gigen along the Iskar River; Montana along the Ogosta River, while the lowest values were recorded in point of Sadovets village along the Vit River.

3.3. Chemical oxygen demand (COD)

Another important factor for the water quality is the indicator **chemical oxygen demand** (COD). The chemical oxygen demand is a measure of the total quantity of oxygen required for oxidation of all organic matter (organic available, inert organic material) to carbon dioxide in the water and oxidizable organic substances. The oxidation is carried out by chemical oxidants. There are several different types of oxidation using dichromate, permanganate and iodate. Highest oxidation state is achieved by the dichromate method. In practice, for less contaminated waters the most used is the permanganate method and for more contaminated waters – dichromate method. Consumption of chemicals is a proxy for organic matter and the quantity of oxygen required. This indicator determines the overall water pollution. COD values are always higher than the BOD values, since this test oxidized organic material inert and biologically available organic matter. Fig. 6 presents the average values of COD – Mn along rivers for the 5 years period 2009–2013. The highest values were registered in the Ruse Lom River. In this valley, at the point of Basarbovo were reported significantly higher values than the average. The lowest averages were recorded along the Vit River.

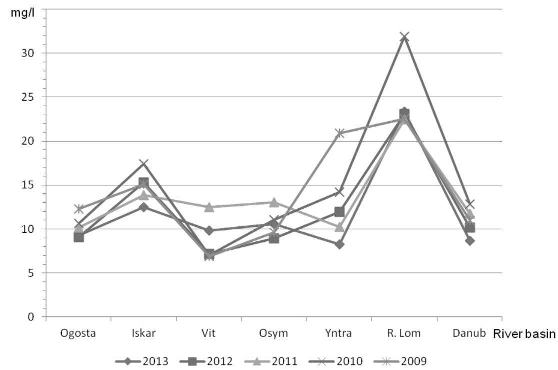

Figure 6: Chemical oxygen demand (COD) in river basins

3.4. Nutrients

Important for the quality of surface waters are nutrients: **Ammonium nitrogen** (NH_4^+). It is a major cause of eutrophication of water, and in high concentrations is toxic for aquatic organisms; **Nitrate nitrogen** (NO_3^-) – stimulates the growth of aquatic plants and **Orthophosphate** (PO_4^{3-}) – they are the main source for the growth of aquatic plants in photosynthesis, but in excessive amounts leads to algae blooms.

Nutrients are a supportive unit in the process of primary productivity in aquatic ecosystems. Under optimal temperature and light, they assimilate quickly, which often leads to the eutrophication of water, with concomitant adverse effects (oxygen deficit, mortality of bottom hydrobionts, etc.). The most important role in these processes has the mineral nitrogen in three states and phosphates. Increase in their concentration in the water is considered to be an indicator of organic pollution. Ammonia and nitrite in the water are the most harmful forms of nitrogen compounds. The presence of free flowing ammonia in the water is an indicator for fresh contamination from human and animal waste as it is produced as its end product in the course of anaerobic catabolic processes associated with the decomposition of nitrogen-containing organic compounds in organic waste. The presence of nitrates in the water, on one hand, is usually due to an organic or fresh fecal contamination (product of oxidation of the ammonium ions in the medium by aerobic nitrifying bacteria) and on the other hand - to the result of the contamination of the water with inorganic substances coming usually from agriculture and industry.

Increased content of ammonium nitrogen (NH_4^+) over 0.6 mg/dm^3 is reported in the valleys of the Iskar River in the monitoring points Vladayska, Kakach, Malak Iskar, Lesnovska. Also the same increased content is reported for the Osam River with its tributaries and for the Shawarna River and Lomia River. For the valley of the Vit River near the village of Opanets in Tuchenica River before inflowing into Vit River there is increased content of NH_4^+, too.

Increased rates of nitrate nitrogen (NH_4^+) are reported in the Cherni Lom River, in the Ostritza village, and Cherven and Pisanets villages in Beli Lom River from along the Ruse Lom River. In these respects it varies from $6-10\,mg/l$. High values are reported also in the Tsaratsar River in the point near Maluk Porovec village and in Chayrlak River in the points near Cherkovna village from along the Dobrudza rivers. High values are also recorded in the Iskar River at points near Luki, from the valley of the Iskar River and in Studena River at the point Shoseen most before inflowing into the Yantra River.

According to DRBU [7], high levels of orthophosphate (PO_4^{3-}) 2.4 mg/l are reported for more than a half of the valleys of the Bulgarian Danube River Basin: the Iskar River – in Roman and Rebarkovo; the Ogosta River valley; the Skat River – in Miziya and Byala Slatina; Ruse Lom valley and its tributaries – in Pisanets, Ostritza, Beli Lom and Cherven village; along the Yantra River and points near Nov grad; at the point of Studena River – a right tributary of Yantra River, the value is 2.4 mg/l also. Even the bigger value of 0.425 mg/l exists in the Danube town of Ruse and Chairlak River near Cherkovna village.

Classification of ecological status of rivers is shown on Fig. 7. This classification is made on the base of IMPRESS group for estimation of the ecological risk. The main classification indicators in IMPRESS system are: oxygen regimes, nutrients, sulphates, chlorides and metal ions [6].

4. Conclusions

It is well known that there are two main types of river pollutions – **from point sources** and **from ship waste waters**. Main water pollutions are such as: discharge of urban sewage settlements with over 2000 equivalent citizens; discharging without necessary treatment; discharges from urban waste water treatment; discharges of industrial waste water from the big industrial cities.

Despite all adopted regulations and agreements between Danube countries,

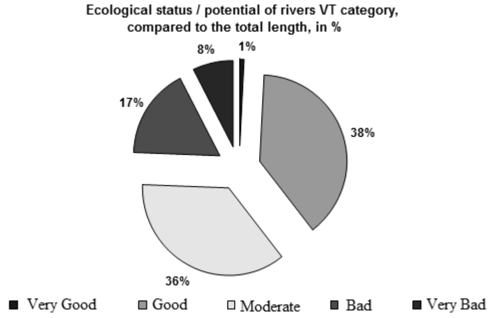

Figure 7: Ecological status of the rivers compared to the total length in %

the Danube River is still polluted by both of point sources and unregulated disposal of ship waste waters.

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