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An Example of the Adverse Impacts of Various Anthropogenic Activities on Aquatic Bodies: Water Quality Assessment of the Provadiyska River (Northeastern Bulgaria)

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Abstract

Anthropogenic activities deteriorate the quality of water resources, which reduces their socio-economic suitability, endangers public health, and affects aquatic life. This work presents the results of physicochemical monitoring of the Provadiyska River (Northeastern Bulgaria) and aims to assess water quality status according to the guidelines pointed out in the National regulatory standard – Regulation H-4/2012 for characterization of the surface waters. The selected river has become one of the most seriously polluted streams in the territory of the country due to the effect of various human practices occurring in the drainage basin, such as agriculture, industry, and urban development. Data about the values of ten physicochemical variables (pH, EC, DO_2, N-NH_4, N-NO_3, N-NO_2, N-tot, P-PO_4, P-tot, and BOD_5), recorded at four measuring points during the period 2015–2020 have been used. Results obtained indicate that almost all of the parameters considered do not meet the reference norm for "Good status", thus water quality could be assessed as "Moderate". Failed variables appear to be EC, N-NH_4, N-NO_3, N-NO_2, N-tot, P-PO_4, P-tot, and BOD_5 whose highest observed content remains from two up to nine times above the maximum permissible limits of Regulation H-4/2012. Water contamination arises from different sources and activities, including the excessive fertilization of croplands, the unregulated release of animal manure from livestock farms, the uncontrolled discharge of municipal and industrial effluents into the river, etc. The expansion of sewerage systems in the settlements, the construction of wastewater treatment facilities, as well as the adoption of codes for best farming practices are among the most important actions that should be taken to reduce the deleterious effects of various anthropogenic activities on water quality.

Keywords: water quality; water pollution; human impact; Bulgaria

Introduction

Water, a prime natural resource and precious social asset, forms habitats for aquatic species, serves vital human needs, and at the same time plays an increasingly important role in various sectors of the global and national economy. As a result of this multipurpose use, water quality suffers from a range of anthropogenic activities like agriculture, urban development, industry, etc. Agriculture provides employment to millions of people and is responsible for feeding the growing world's population (Kernebeek et al., 2016). However, some farming practices, such as the excessive usage of fertilizers and pesticides, enrich surface water bodies with nitrogen and phosphorus, which causes structural changes in the freshwater ecosystems and

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provokes eutrophication (Chislock et al., 2013, Withers et al., 2014, Dodds & Smith, 2016, Romanelli et al., 2020). The expansion of urban regions due to the rapidly rising population also brings environmental issues. The untreated or inadequately treated municipal effluents contain fecal coliforms and so import pathogenic bacteria into the waters. Such microbial organisms pose a serious threat to public health (Mills et al., 2018, Nazemi et al., 2018). Industrial wastewaters inflict no less harmful effects. Two examples include the chemical factories emitting synthetic materials and the mining enterprises releasing heavy metals into the rivers. Those substances often engender intoxication and hide carcinogenic risks, so their presence in the aquatic bodies is an issue of great concern (Mohammadi et al., 2019, Ravindra & Mor, 2019, Sall et al., 2020).

The implementation of the Water Framework Directive (WFD) 2000/60/EC of the European Parliament and the Council of 23 October 2000 requires all EU member states to protect and improve the quality of their surface and sub-surface water resources, so that all streams, lakes, and aquifers achieve "Good status" at the latest by 2027. Currently, five years before the stated deadline, the implementation of the mentioned objective seems to be a difficult task. Although a set of rules, measures, and action programs in this field were prepared by decision-makers and stakeholders during the last two decades, about 40% of the EU waters still do not meet the requirements. One of the main obstacles hindering the European states to achieve the WFD's target remains the anthropogenic influence on the aquatic streams (Vilmin et al., 2018).

Bulgaria is among the European countries with most dramatically declining population and shrinking economy during the last decades. As a result of those socio-economic processes, the human impact on the environment gradually weakens and a lot of water bodies tend to improve their quality (Varbanov & Gartsiyanova, 2015, Seymenov, 2019). However, some regions in the territory of the country continue to be pressured by various anthropogenic activities and so critically contaminated rivers can still be established (Radeva & Seymenov, 2021). One such example includes the Provadiyska River, which has been classified as "an ecological hot-point with seriously polluted sections" due to the discharge of wastewater products from farmlands, settlements, and industrial enterprises. Gartsiyanova (2016) reported elevated concentrations of ammonia ions, nitrates and nitrites in the river waters for the period 1993–2014. The annual bulletins published by the Executive environment agency between 2000 and 2018 concerning the ecological status of the rivers in the Black Sea drainage area showed severe contamination with increased values of suspended solids, nitrates, phosphates, and organic matter as a result of the direct discharge of untreated municipal and industrial effluents into the stream channel.

Thus, this work aims to assess the water quality status of the Provadiyska River in compliance with the reference norms pointed in Regulation H-4/2012 for characterization of the surface waters. The realization of the stated objective is expected to update the existing knowledge from previous investigations with new data for a more contemporary period.

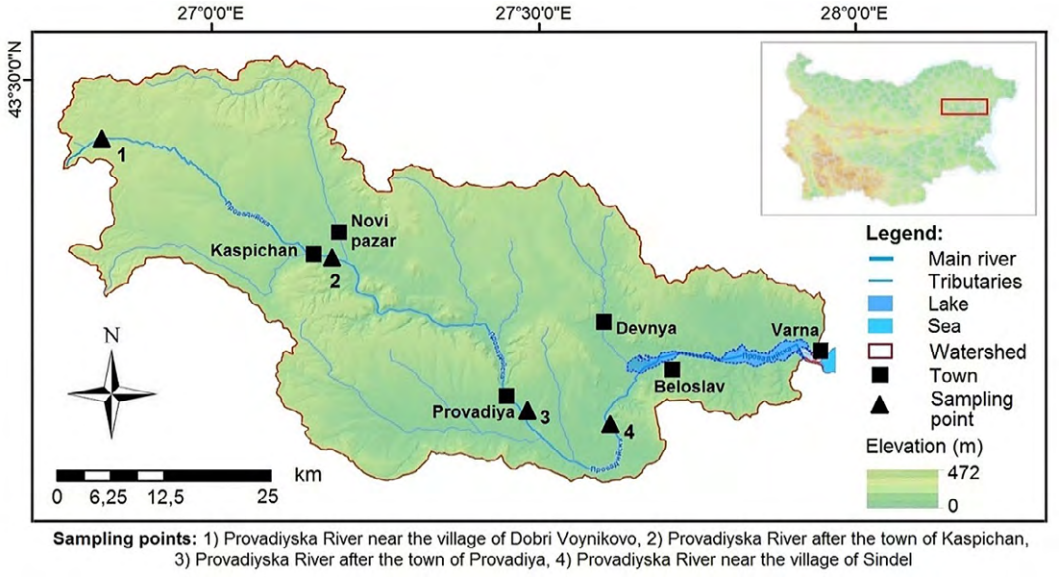
Study area

The Provadiyska River is a watercourse in the northeastern section of Bulgaria, which flows in a length of 119 km and has a drainage basin of 2132 km². The investigated stream originates from the eastern slopes of the Samuil hills in the Eastern Danube Plain at an altitude of 441 m above sea level, later runs southeast and northeast, and empties into the Beloslav Lake, which is connected with the Varna Lake, which in turn drains into the Black Sea (Figure 1).

The hydrological features of the Provadiyska River at the gauging station near Sindel include a mean annual flow 2.33 m^3/s. The high runoff phase occurs from February to April, while the low discharge period is most typical between August and October (Hristova, 2012).

Data and methods

Statistical information about the values of ten physicochemical variables has been used. Data concern the measured content of the following parameters: pH, electrical conductivity (EC), dissolved oxygen (DO_2), ammonium nitrogen ($N\text{-}NH_4$), nitrate nitrogen ($N\text{-}NO_3$), nitrite nitrogen ($N\text{-}NO_2$), total nitrogen (N-tot), orthophosphates ($P\text{-}PO_4$), total phosphorus (P-tot), and five-day biochemical oxygen demand (BOD_5), in-situ collected and then processed in an accredited laboratory following a standardized procedure. The measurements were carried out by the Executive environment agency at four sampling points during the period 2015–2020 with a frequency of the observations four times per year. The monitoring sites,



Sampling points: 1) Provadiyska River near the village of Dobri Voynikovo, 2) Provadiyska River after the town of Kaspichan, 3) Provadiyska River after the town of Provadiya, 4) Provadiyska River near the village of Sindel

Figure 1. Map of the relief and drainage network showing the location of sampling points

falling within surface water bodies of type R4: Semi-mountain rivers in a Pontic province (a measuring point near the village of Dobri Voynikovo) and R11: Small and medium Black Sea tributaries (monitoring sites after the towns of Kaspichan and Provadiya, and near the village of Sindel), have been selected so that cover parts of upstream, midstream, and downstream reaches of the Provadiyska River (Figure 1). Water quality status has been analyzed following the guidelines of the National regulatory standard – Regulation H-4/2012 for characterization of the surface waters (Table 1). The term "water pollution" will be used in this paper when the value of a given physicochemical parameter does not meet the reference norms for "good" and "excellent" status, recommended in Regulation H-4/2012.

Descriptive statistics, i.e. minima, maxima and means, calculated for each variable have been presented in the first stage of the work. Water quality has been related to the land use/land cover structure. For this purpose, a map of the CORINE land cover in the Provadiyska River basin has been made using the database of COPERNICUS Land Monitoring Services (2018).

Table 1. Reference values of physicochemical parameters at different water body types as pointed out in Regulation H-4/2012 for characterization of the surface waters

Water body types	Water quality status	Water quality parameters									
		pH	EC, µS/cm	DO_2, mg/l	$N\text{-}NH_4$, mg/l	$N\text{-}NO_3$, mg/l	$N\text{-}NO_2$, mg/l	N-tot, mg/l	$P\text{-}PO_4$, mg/l	P-tot, mg/l	BOD_5, mg/l
R4	Excellent	–	<700	>8.0	<0.04	<0.5	<0.01	<0.5	<0.02	<0.025	<1.2
	Good	6.5–8.5	700–750	8.0–6.0	0.04–0.4	0.5–1.5	0.01–0.03	0.5–1.5	0.02–0.04	0.025–0.075	1.2–3.0
	Moderate	–	>750	<6.0	>0.4	>1.5	>0.03	>1.5	>0.04	>0.075	>3.0
R11	Excellent	–	<850	>6.0	<0.3	<1.0	<0.03	<1.0	<0.07	<0.15	<2.0
	Good	6.5–8.5	850–900	6.0–5.0	0.3–0.65	1.0–2.5	0.03–0.06	1.0–2.5	0.07–0.15	0.15–0.3	2.0–5.0
	Moderate	–	>900	<5.0	>0.65	>2.5	>0.06	>2.5	>0.15	>0.3	>5.0

Results

The physicochemical parameter ***pH*** is a measure informing about the active reaction of water (acidic, neutral, or alkaline). The possible numerical range varies from 0 up to 14. Generally, values less than 7 mean an acidic reaction; numbers equal to 7 indicate a neutral reaction, and ratings greater than 7 reveal an alkaline reaction. The value of this variable depends on some natural conditions. For instance, river waters

flowing over karst terrains with limestone rocks are more often alkaline, unlike those running through volcanic and metamorphic formations that are chiefly acidic. In addition, the wastewaters from mines and metallurgical enterprises usually decrease the values of pH. Neutral to weakly alkaline water is considered to be most suitable for aquatic life and human use (Omer, 2019). Results obtained show that the waters of the Provadiyska River are characterized by neutral to slightly alkaline reaction (Table 2). A possible explanation of this result gives the significant share of sedimentary rocks, as well as the lack of ore mines in the drainage basin. Frequency analysis indicates that from 90.9% (the Provadiyska River after Kaspichan) to 100.0% (the Provadiyska River near Dobri Voynikovo and after Provadiya) of the collected samples fall within the numerical range for "Good status" recommended in Regulation 4/2012 (Figure 2).

Electrical conductivity (EC) is a physicochemical parameter showing the ability of water to conduct electricity. Waters are among the natural resources that are electrical conductors, but this property is influenced by multiple factors like turbidity, mineralization, lithology, and land use. The increased values of EC usually do not cause great concerns because they are often a reflection of natural conditions, such as the presence of calcium ions, which seems to be closely linked to lithology. However, some unsustainable anthropogenic practices like the unregulated disposal of solid or chemical wastes can also provoke increased electrical conductivity (Omer, 2019). The measurements show that the waters of the Provadiyska River are characterized by an elevated ability to conduct electricity (Table 2). The lowest values are established at the sampling sites near Dobri Voynikovo and after Kaspichan. On the other hand, the highest levels are recorded at the measuring sites after Provadiya and near Sindel. Frequency analysis gives the following information: from 7.7% (the Provadiyska River after Provadiya) to 87.5% (the Provadiyska River near Dobri Voynikovo) of the collected samples achieve "Excellent status". Excluding the sampling points near Dobri Voynikovo and after Provadiya, where no values within the numerical range for "Good status", in the rest measuring sites between 4.3% (the Provadiyska River at Sindel) and 4.5% (the Provadiyska River after Kaspichan) of all tests fall into "Good status". Increased values of EC are established at all measuring sites, so between 9.1% (the Provadiyska River after Kaspichan) and 92.3% (the Provadiyska River after Provadiya) of the samples could be assessed into "Moderate status" following the norms of Regulation 4/2012 (Figure 2).

Table 2. Descriptive statistics of the values of physicochemical variables in the surface waters

River – water sampling point	Values	pH	EC, µS/cm	DO_2, mg/l	N-NH_4, mg/l	N-NO_3, mg/l	N-NO_2, mg/l	N-tot, mg/l	P-PO_4, mg/l	P-tot, mg/l	BOD_5, mg/l
Provadiyska – Dobri Voynikovo	Minimum	8.03	578	7.00	0.22	3.50	0.02	3.50	0.05	0.08	1.58
	Average	8.25	638	9.14	0.53	8.24	0.06	9.18	0.06	0.13	4.50
	Maximum	8.48	810	10.60	1.10	11.70	0.15	12.10	0.08	0.19	8.40
Provadiyska – after Kaspichan	Minimum	7.26	458	3.00	0.05	1.13	0.04	1.60	0.03	0.10	1.32
	Average	8.14	709	8.55	0.62	5.98	0.11	7.62	0.10	0.25	4.65
	Maximum	8.66	990	14.20	2.50	13.20	0.50	15.10	0.50	0.90	12.00
Provadiyska – after Provadiya	Minimum	7.72	760	5.52	0.08	2.21	0.03	2.68	0.04	0.09	1.51
	Average	8.04	1163	7.93	0.46	5.64	0.07	6.49	0.20	0.28	2.87
	Maximum	8.32	1590	10.20	1.91	9.69	0.12	9.81	0.53	0.66	6.30
Provadiyska – Sindel	Minimum	7.47	723	3.57	0.03	3.16	0.02	3.20	0.03	0.06	0.70
	Average	8.18	1252	7.84	0.23	6.34	0.11	6.72	0.21	0.27	2.48
	Maximum	8.67	2606	11.89	1.11	11.40	0.46	11.80	0.55	0.78	7.30

Dissolved oxygen (DO_2) is a measure showing the amount of oxygen that is present in water. Surface water bodies absorb and dissolve a part of the available oxygen in the lowest layer of the atmosphere. The presence of sufficient oxygen in water maintains aquatic life and protects natural habitats. However, unfavorable hydro-ecological conditions, such as eutrophication, can critically reduce the dissolved oxygen levels (Omer, 2019). The lower oxygen saturation usually leads to suffocation and death of aquatic species, which is closely related to the loss of biodiversity in the aquatic ecosystems. The resulting information reveals that the waters of the Provadiyska River almost do not suffer from oxygen deficit (Table 2). Two exceptions are the monitoring sites after Kaspichan and near Sindel, where 13.9% and 4.3% of all samples remain under the reference range for "Good status". Regarding

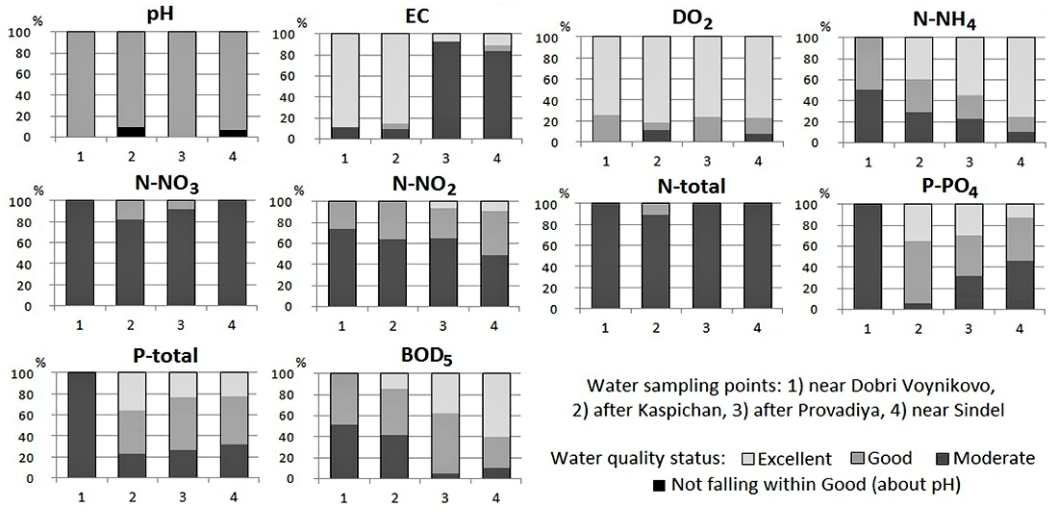


Figure 2. Frequency (% of all samples) of water quality variables in a certain status according to the reference values stated in Regulation H-4/2012 for characterization of the surface waters

all analyzed water measuring points, from 4.3% (after Kaspichan) up to 25.0% (near Dobri Voynikovo) of the collected tests fall in "Good status", while between 75.0% (near Dobri Voynikovo) and 81.8% (after Kaspichan) of the recorded samples achieve "Excellent status" according to Regulation 4/2012 (Figure 2).

Ammonium nitrogen (N-NH_4) is a chemical compound of ammonia – a colorless gas with a pungent smell and one of the three inorganic nitrogen forms (the other two include nitrates and nitrites). Ammonia and its compounds are released as a result of the decomposition of organic matter by aerobic bacteria during the microbiological process of ammonification. The elevated concentrations of ammonium nitrogen in water bodies usually indicate an inflow of sewerage wastewaters or livestock farming effluents containing excrements, urine, and liquid manure. Ammonia and its compounds are able to inflict toxic effects on freshwater ecosystems (Omer, 2019). Results show the waters of the Provadiyska River suffer from ammonia pollution (Table 2). Excluding the monitoring point near Dobri Voynikovo, where no values in the numerical range for "Excellent status", frequency analysis reveals that in the rest measuring sites from 40.9% (after Kaspichan) to 73.9% (near Sindel) of the collected tests achieve the best status. Between 17.4% (near Sindel) and 50.0% (near Dobri Voynikovo) of the samples fall in "Good status", and from 8.7% (near Sindel) to 50.0% (near Dobri Voynikovo) of the recorded tests could be assessed into "Moderate status" in accordance with Regulation 4/2012 (Figure 2).

Nitrate nitrogen (N-NO_3) is a chemical compound of the nitrate – a water-soluble salt of the nitric acid and one of the three inorganic nitrogen forms (the other two include ammonia and nitrites). Nitrates are formed as a result of the oxidation of ammonia ions by aerobic bacteria during the microbiological process of nitrification. Nitrates are not toxic substances, but under certain conditions, it is possible to transform into carcinogenic nitrosamines (nitrites). Nitrate pollution almost always indicates an inflow of soil runoff saturated with chemical agents like artificial fertilizers, pesticides, and plant protection products, which continue to be widely used for agricultural purposes. Those products are applied onto arable lands in order to be achieved an accelerated yield of crops or the same crops to be protected from pests, but their excessive dispersal causes unfavorable effects on water quality (Withers et al., 2014). Results obtained show the waters of the Provadiyska River suffer from significant nitrate pollution (Table 2). The measured maximum content of this variable exceeds the reference norm for "Good status" at all monitoring points. Most severe is the contamination at the water sampling site after Kaspichan, where the highest observed value is almost six times above the maximum permissible limit. Frequency analysis indicates that samples falling in the numerical range for "Excellent status" are not recorded. Between 81.8% (after Kaspichan) and 100.0% (near Dobri Voynikovo and near Sindel) of the tests could be assessed in "Moderate status", which reveals permanent nitrate contamination (Regulation 4/2012) (Figure 2).

Nitrite nitrogen (N-NO_2) is a chemical compound of the nitrite – a water-soluble salt of the nitrous acid and one of the three inorganic nitrogen forms (the other two include ammonia and nitrates). Nitrites originate from nitrates that have been transformed under certain conditions like acidic pH or increased temperature. A further chemical reaction of the nitrite with amines forms nitrosamines – carcinogenic substances, which can inflict toxic or mutagenic effects on aquatic ecosystems and human health (Omer, 2019). Consequently, the presence of nitrites in waters

is an issue of great concern. The sources of nitrite nitrogen in the watercourses include discharges of domestic, industrial, and agricultural effluents, which have been nitrate polluted. Later, under some conditions, a part of those nitrates have been transformed into nitrites. The resulting data reveals that the waters of the Provadiyska River are polluted with nitrite nitrogen (Table 2). The measured maximum levels of this variable exceed the highest permissible limit for "Good status" at all sampling points. Therefore, from 52.2% (near Sindel) to 75.0% (near Dobri Voynikovo) of the collected tests could be assessed into "Moderate status". Frequency analysis also shows that from 23.1% (after Provadiya) up to 39.1% (near Sindel) of all tests fall within the numerical range for "Good status" following Regulation 4/2012 (Figure 2).

Total nitrogen (N-tot) is a physicochemical parameter showing the overall content of nitrogen in the waters – both in the form of inorganic compounds (ammonia, nitrates, and nitrites) and as an organic substance as well. Nitrogen is an essential nutrient for aquatic ecosystems, but its increased content causes adverse hydro-ecological effects (Omer, 2019). Although nitrogen is naturally occurring in environment, water pollution is often provoked by human activities. The untreated municipal wastewaters, as well as the chemicals, which are often dispersed onto arable lands, appear to be among the leading causes of nitrogen contamination (Withers et al., 2014). The conducted measurements indicate that the waters of the Provadiyska River seem to be seriously loaded with respect to nitrogen (Table 2). The maximum values of this parameter exceed the highest permissible limit for "Good status" at all monitoring sites. Most polluted are the waters of the river after Kaspichan, where the highest content is about seven times higher than the reference norms. Frequency analysis shows that 9.1% of the measured concentrations at the Provadiyska River after Provadiya achieve "Good status", while values falling within this numerical range in the rest of the monitoring points are not established. Between 90.9% (after Provadiya) and 100.0% (near Dobri Voynikovo, after Kaspichan, and near Sindel) of the tests could be categorized into "Moderate status" according to Regulation 4/2012 (Figure 2).

Orthophosphates (P-PO_4) are water-soluble salts of orthophosphoric acid. Orthophosphates are nutrient components naturally presenting at low levels in waters, soils, and plants. However, increased values of orthophosphates in the rivers can cause an overgrowth of algae, resulting in algal blooms and eutrophication. The process of eutrophication blocks sunlight, decreases oxygen amounts, and so affects aquatic life (Withers et al., 2014). The pollution sources could be both natural (like soil erosion) and human-induced (as uncontrolled disposal of agricultural and domestic effluents containing phosphorus-rich fertilizers and laundry detergents). Results show the waters of the Provadiyska River are contaminated with orthophosphates (Table 2). The highest observed values seem to be higher than the maximum permissible limit for "Good status" at all monitoring sites. Frequency analysis confirms this statement and reveals between 4.5% (after Kaspichan) and 100.0% (near Dobri Voynikovo) of all tests could be assessed into "Moderate status". Excluding the sampling site near Dobri Voynikovo, where no values in the numerical range for "Good status" and "Excellent status", in the rest measuring points: from 38.5% (after Provadiya) up to 59.1% (after Kaspichan) of the collected tests achieve "Good status", and between 7.7% (after Provadiya) and 36.4% (after Kaspichan) of all samples fall within "Excellent status" in accordance with the guidelines of Regulation 4/2012 (Figure 2).

Total phosphorus (P-tot) is a physicochemical parameter informing about the overall content of phosphorus and its compounds in the waters – both as inorganic salts (like phosphates and orthophosphates) and as an organic substance. Phosphorus is a nutrient with an essential role for plant and animal growth. However, elevated values of this parameter cause an overgrowth of algae, which provokes structural changes in aquatic ecosystems and leads to eutrophication (Withers et al., 2014). Water pollution with phosphorus comes from some natural processes occurring in the drainage basin (such as soil erosion or weathering of phosphorus-containing rocks) and anthropogenic activities as well (like unregulated disposal of untreated agricultural and household wastewaters). The conducted measurements show the waters of the Provadiyska River appear to be polluted with regard to phosphorus. The highest observed content remains above the maximum permissible limit for "Good status". Frequency analysis confirms this result and informs: from 22.7% (after Kaspichan) up to 100.0% (the near Dobri Voynikovo) of all tests fall into "Moderate status". Excluding the monitoring site near Dobri Voynikovo, where no values falling in the numerical range for "Good status" and "Excellent status", in the rest measuring points between 40.9% (after Kaspichan) and 53.8% (after Provadiya) of the samples achieve "Good status", and from 21.7% (near Sindel) up to 36.4% (after Kaspichan) of all tests could be categorized into "Excellent status" following Regulation 4/2012 (Figure 2).

Biochemical oxygen demand (BOD_5) is a measure showing the amount of dissolved oxygen consumed by aerobic bacteria and microorganisms while they decompose organic matter over a specific time period (five days). Microorganisms living in surface

water bodies use oxygen to support their vital and metabolic processes, but under some circumstances, such as nutrient enrichment and eutrophication, microbial metabolism consumes dissolved oxygen in a larger amount than normal (Omer, 2019). The problem arises from the fact that aquatic species may die if oxygen is depleted by microbial metabolism. The lack of sufficient oxygen in water due to its excessive consumption by aerobic bacteria results in long-term hypoxia, which causes a loss of biodiversity and degradation of the aquatic ecosystem. Therefore, biochemical oxygen demand is often used as an indicator of the overall degree of water contamination with organic matter (Omer, 2019). Results show the waters of the Provadiyska River are characterized by increased biochemical oxygen demand (Table 2). The highest values of this variable exceed up to three times the reference norms for "Good status", meaning the river waters suffer from significant organic pollution. Frequency analysis shows that from 7.7% (after Provadiya) up to 50.0% (near Dobri Voynikovo) of all tests could be assessed into "Moderate status", between 26.1% (near Sindel) and 53.8% (after Provadiya) of the recorded samples fall in the numerical range for "Good status", while from 13.6% (after Kaspichan) up to 60.9% (near Sindel) of the collected tests achieve "Excellent status" according to Regulation 4/2012 (Figure 2).

Discussion

Compared to a previous research article, the results obtained in the current work demonstrate a lot of similarities, but highlight some differences as well. Gartsiyanova (2016) explored water quality of the rivers in the Black Sea drainage basin in Bulgaria during the period 1993–2014. The cited author reported that the Provadiyska River is the most contaminated watercourse in the investigated territory. The leading pollutants before its mouth include nitrate nitrogen and nitrite nitrogen – the average values of those parameters are 5.08 mg/l and 0.21 mg/l, while the maximum levels reach 16.50 mg/l and 0.45 mg/l, respectively (Gartsiyanova, 2016). The resulting data in this work establishes a slightly lower maximum content of nitrate nitrogen, but higher average values. Respecting nitrite nitrogen, the mean concentrations calculated in the present paper appear to be lower than those in the cited study, but the highest observed values remain approximately the same (Table 2). In addition, in the annual bulletins of the Black Sea basin directorate concerning the ecological conditions of the surface waters in the period from 2000 to 2018, the Provadiyska River was defined as "an ecological hot-point with increased values of various chemical parameters". The obtained results in the current research reveal an analogous situation. All this suggests the waters of the Provadiyska River do not significantly improve their quality and continue to be seriously polluted during the period 2015–2020. The failed variables at all sampling points are ammonia nitrogen, nitrate nitrogen, nitrite nitrogen, total nitrogen, orthophosphates, phosphorus, and biochemical oxygen demand whose highest content exceeds from two up to nine times the maximum permissible limits for "Good status", recommended in Regulation 4/2012 for characterization of the surface waters. In contrast, the pH-value and the dissolved oxygen level remain mostly within the reference norm (Table 2). The analysis of the territorial distribution in the content of the physicochemical variables does not find any spatial changes along the length of the river. Most of the parameters considered maintain relatively similar concentrations or demonstrate unsustainable increase/decrease of the values from one sampling site to another without a clearly expressed direction of change. An exception is an electrical conductivity whose values obviously increase from upstream to downstream part.

Water quality is a reflection of natural processes and anthropogenic activities occurring in the river basin. A detailed picture of spatial distribution of both primary and human-transformed landscapes in a given catchment area gives the land use/land cover structure. The predominant land cover class in the study region is "Non-irrigated arable lands", which occupies 72.4% of the total area. Some of the rest most character lands include "Forest" (14.3%), "Urban areas" (3.6%), "Shrub and/or herbaceous vegetation" (3.2%), "Industrial units" (2.3%), "Permanent crops" (1.9%), while the other classes have a smaller relative share (Figure 3). In short, there is a significant predominance of human-transformed landscapes. The drainage basin of the Provadiyska River is traditionally pressured by anthropogenic activities, such as agriculture, industry, and urban development. The Eastern Danube Plain is occupied by farmlands with cereal and technical crops, while the foothills of the Provadiya Plateau and the Frangen Plateau are covered by vineyards and orchards. In addition, a lot of livestock farms exist in the vicinity – e.g. the swine-breeding complex near the village of Avren, the poultry farm near the town of Devnya, etc. The Provadiyska River basin concentrates a total of 113 settlements, including the third most populated town in Bulgaria – Varna with a population of about 330 000 people,

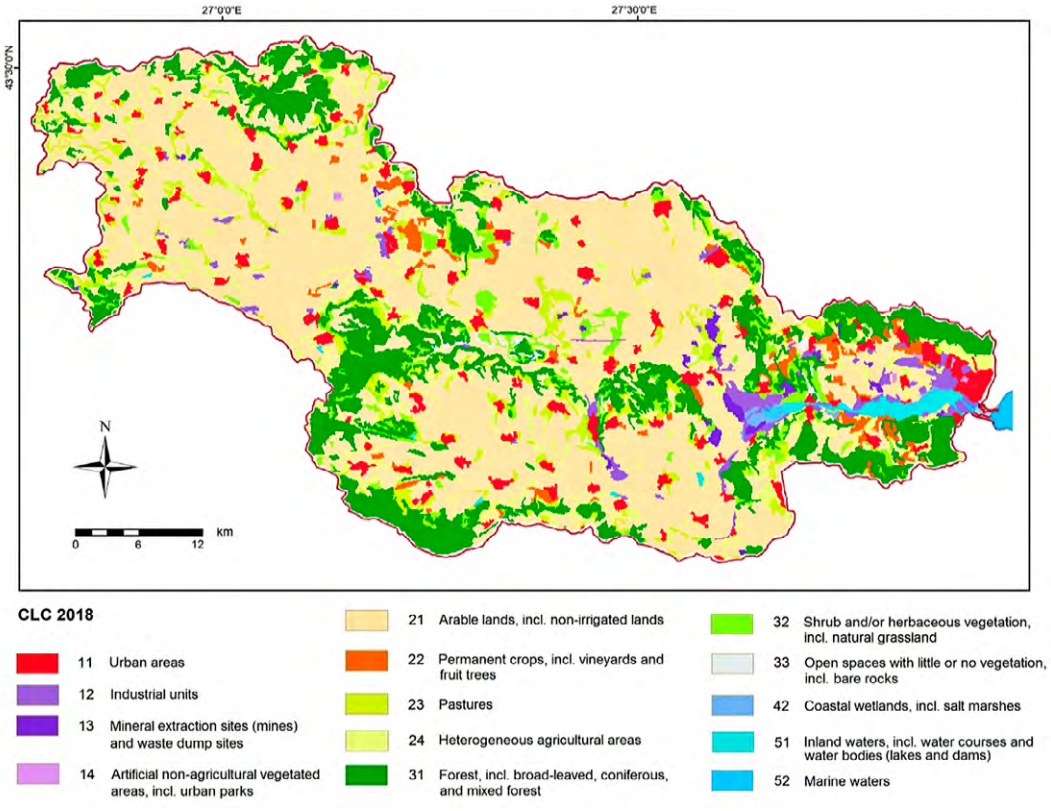


Figure 3. CORINE Land Cover (2018) of the Provadiyska River basin

smaller cities like Kaspichan, Novi pazar, Provadiya, Devnya, and Beloslav, as well as over 100 villages (Figure 1). The agglomeration of Varna, which attracts almost 25–30 km from the surrounding territories, is a highly industrialized zone with some of the largest enterprises in the Balkan Peninsula. In this region operate cement, glass, porcelain, and faience production factories (near Kaspichan and Novi pazar), a synthetic soda ash production site and an artificial fertilizer enterprise ("Solvay sodi" and "Agropolychim" near Devnya), a salt mine ("Provadsol" near Provadiya), a coal-fired thermal power plant ("Varna Power Plant") (Figure 3). Moreover, three agglomerations (Kaspichan, Novi pazar, and Beloslav) with a population equivalent of greater than 2000 people still are not connected to sewage systems and thus they do not meet the requirement of Directive 91/271/EEC concerning the collection, treatment, and discharge of wastewaters released from urban areas and certain industrial sectors. Consequently, water pollution originates from many sources. The leading polluting activities include the excessive fertilization of the arable lands, the unregulated disposal of animal manure from the livestock farms, the uncontrolled deposition of solid wastes into illegal rubbish dumps, as well as the widespread discharges of household and industrial effluents from the settlements with a lack of public sewerage network and wastewater treatment facilities.

Conclusion

The conducted analysis, based on the recorded values of ten physicochemical variables at four sampling points in the period 2015–2020, shows that almost all of the parameters considered do not meet the reference norms for "Good status", recommended in the National regulatory standard – Regulation 4/2012 for characterization of the surface waters. The failed variables at all monitoring sites include ammonium nitrogen ($N\text{-}NH_4$), nitrate nitrogen ($N\text{-}NO_3$), nitrite nitrogen ($N\text{-}NO_2$), total nitrogen (N-tot), orthophosphates ($P\text{-}PO_4$), total phosphorus (P-tot), and biochemical oxygen demand (BOD_5) whose maximum concentrations remain from two up to nine times above the highest permissible limits stated in Regulation 4/2012. Thus, water quality could be assessed as "Moderate" regarding those parameters. Compared to a previous study, the resulting information in this work shows a partly similar situation and suggests that the Provadiyska River is one of the most seriously and permanently polluted watercourses in the territory of Bulgaria during the last three decades. Water contamination is due to the

effect of various anthropogenic activities occurring in the catchment area, especially agriculture, urban development, and industry. The unregulated disposal of untreated effluents from arable lands, livestock farms, urban and rural settlements, and industrial units is a major issue. Construction of public sewage network and wastewater treatment infrastructure in the agglomerations with a population equivalent of greater than 2000 people to remove the release of raw municipal and industrial wastes is strongly recommended. In order to abate the agricultural pollution, it is necessary to reduce the excessive dispersal of fertilizers and pesticides onto croplands through the promotion of sustainable farming practices. The implementation of the listed advices could improve water quality, which would protect human health and aquatic life. The results obtained supplement previous research articles and provide valuable information for a recent period. In future, this study could be extended by calculating water quality indices.

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