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Impact of the coal fired power plants on two rivers in Bulgaria

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Abstract. This paper presented the effect of the activity of the coal fired power plants „Republika" and „Bobov dol" in Bulgaria and the influence of the wastewaters discharge on the ecological status of Razmetanitsa River (Struma River catchment – West Aegean region) and Sokolitsa River (Maritsa River catchment, East Aegean region). The data of the biological quality elements macrozoobenthos, phytobenthos and fish fauna; basic physicochemical parameters, dissolved oxygen, oxygen saturation, conductivity, biological oxygen demand, ammonium nitrogen, nitrate nitrogen, nitrite nitrogen, total nitrogen, orthophosphates as phosphorus, total phosphorus, calcium (calcium carbonate hardness), total suspended substances; specific pollutants - iron, manganese, copper, zinc, aluminum, chromium total, arsenic, free cyanides, polychlorinated biphenyls, phenols, uranium, radium-226, total α-activity, total β-activity, etc.; sulphates, chlorides; the priority substances cadmium, lead, mercury and nickel from Annex 1 of Directive 2013/39/EU were reviewed and assessed for monitoring sites before and after the discharge points from coal fired power plants in the Struma and Maritsa catchments during the period 2013-2022. A relation between the worsened biological quality elements, the exceeded values of the monitored basic physicochemical parameters and the exceeded environmental quality standards of the specific pollutants and the deterioration of the ecological status of the observed surface water bodies was established.

Key words: coal combustion, wastewater discharge, water pollutants, ecological status.

Introduction

The coal fired power plants (CFPPs) are undoubtedly recognized as one of the main sources of air pollution that harm human health and the environment. Unfortunately, it is less well known that the same CFPPs are both large users and polluters of water (U.S. Environmental Protection Agency (EPA), Press Office, 2023). The main use of water in the activities of CFPP is to condense the steam, i.e. for its cooling. Water is also used to compensate for the high pressure of steam in turbines to generate electricity, to wet and transport the products of coal combustion. The pollutants from coal combustion wastes migrate and contaminate groundwater and surface water, causing degradation of the aquatic ecosystems. This problem is becoming more and more relevant in the time of increasing demand for energy, combined with frequent periods of drought as a manifestation of global climate changes, which requires sustainable management (use and protection) of water resources (EPA, Water office 2015).

According to the Ministry of energetics of Republic of Bulgaria, the quota of electricity

production from CFPPs in Bulgaria in 2020 is 40% and it still takes the biggest part in the structure of the gross production of electricity in Bulgaria by types of power plants. Totally five CFPPs: CFPP "Brikel", CFPP "AES 3C Maritsa East 1", CFPP "Maritsa East 2", CFPP "Contour Global Maritsa East 3" and CFPP "Maritsa - 3" have an impact on Maritsa catchment specifically on four rivers and one dam – Maritsa River, Sokolitsa River, Ovcharitsa River, Sazlijka River, Rozov kladenets Dam. Two CFPPs: CFPP "Bobov dol" and CFPP "Republica" have an impact on Struma catchment specifically on rivers Struma (upper stream, in the region of town of Pernik) and Razmetanitsa (tributary of Dzherman River, middle part of Struma River).

In Bulgaria, recirculation cooling systems (closed cycle) of CFPPs are mainly used. The risk of thermal pollution in the receiving surface water bodies is minimal, but not completely excluded. Residues of chemicals used for disinfection and water purification in cooling system of the CFPP are thrown into facilities designed for the collection of waste water (sludge dump) in the vicinity of the CFPP and most often in the immediate vicinity of a surface water body (Dermendzhieva et al., 2019).

The following environmental risks associated with the production of electricity by CFPPs could be identified:

• During all stages of producing of energy CFPPs waste is generated in huge quantities. In all countries in the world CFPPs can generate thousands to hundreds of thousands of tons of waste each year - most of which is deposited in the immediate vicinity of the same CFPP. There are many CFPPs which have worked for decades, resulting in the disposal and accumulation of billions of tons of coal combustion waste in certain geographic areas (Zhang, 2014);

• The coal combustion waste generated by CFPPs contains certain hazardous pollutants that pose a risk to human health and the environment, including heavy metals such as arsenic, beryllium, boron, cadmium, chromium, lead and mercury and some toxic organic materials such as dioxins and polycyclic aromatics hydrocarbon (PAH) compounds (EPA, 2015).

All these specific pollutants and priority substances directly or indirectly fall into adjacent water bodies or pass through soils into groundwater. This creates a serious danger of toxic pollution with subsequent adverse effects on the aquatic biota and the quality of the affected waters. For all surface water bodies must be achieved good ecological status and good chemical status in accordance with Water Framework Directive (Directive 2000/60/EC) and Directive 2013/39/EC as regards priority substances in the field of water policy. The requirements of the European water legislation Member States to determine of national concern, i.e. river basin specific pollutants and Environmental Quality Standards (EQS) relevant to ecological status of surface water bodies, are transposed in Annex 7 of Bulgarian Ordinance N-4/2012 for characterization of surface waters. The requirements of the European water legislation Member States to transpose Directive 2013/39/EC relevant to chemical status of surface water bodies, are met in Bulgarian Ordinance on environmental quality standards for priority substances and some other pollutants (2010, last amended and supplement 2015).

The aim of this paper is to analyse historical monitoring data of two surface water bodies located in Struma River and Maritsa River catchments (South Bulgaria), which are directly affected by the activity of CFPPs and to assess influence of the wastewaters discharge from existing CFPPs on the ecological status of Razmetanitsa River (West Aegean region) and Sokolitsa River (East Aegean region).

Materials and Methods

Study area

The study area covered surface water bodies located in Struma River catchment (West Aegean region) and Maritsa River catchment (East Aegean region) in South Bulgaria which are affected by CFPP-activities (Fig. 1):

• Surface water body BG4ST600R039, Razmetanitsa River from the sources to the confluence with Dzherman River, Struma catchment, West Aegean region, national river type R13 (small and medium plain Aegean rivers), where are located the fuel facility of CFPP „Bobov dol", "Black Lake" sludge dump and "Kamenik" non-hazardous waste depot with totally 3 points of wastewaters discharge (Fig. 2).

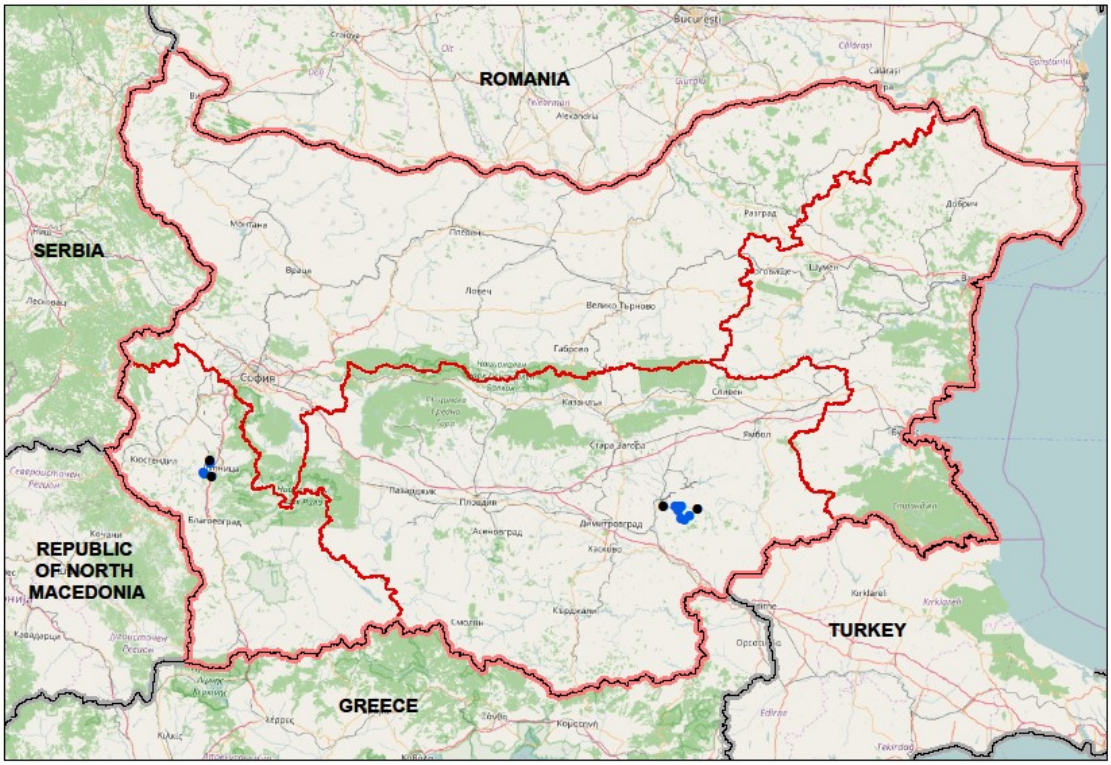

Fig. 1. Location of wastewater discharge points from CFPPs and monitoring sites situated on observed rivers in West Aegean and East Aegean regions in Bulgaria.
Legend: blue circles - points of wastewater discharges from CFPPs; black circles - monitoring sites situated on observed rivers before and after wastewater discharges from CFPPs.

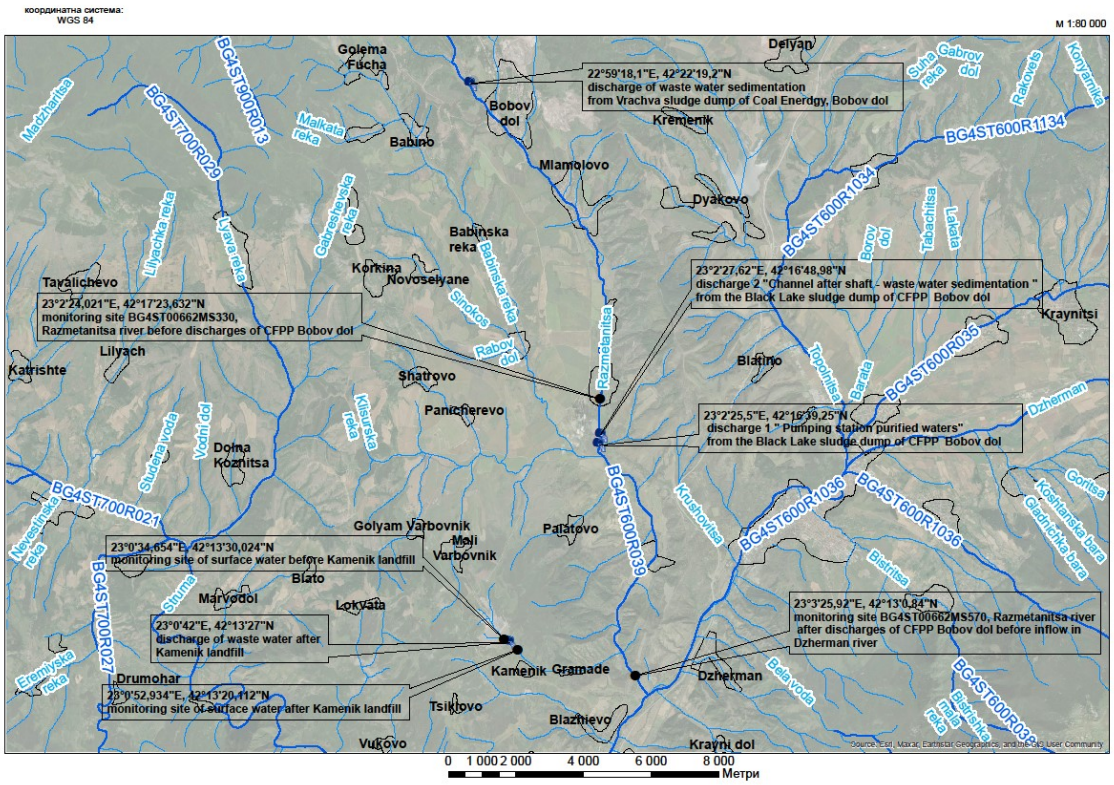

Fig. 2. Wastewater discharge points from CFPP „Bobov dol" facilities and monitoring sites situated on Razmetanitsa River.

• Surface water body BG3MA200R017, Sokolitsa River middle reaches to Rozov kladenets Dam, Maritsa catchment, East Aegean region, national river type R14 (sub-Mediterranean intermittent rivers) where are located the fuel facility of CFPP "Contour Global Maritsa East 3" and Landfill for non-hazardous waste "Embankment Mednikarovo" of "Mines Maritsa East" Ltd with totally 8 points of wastewaters discharge (Fig. 3).

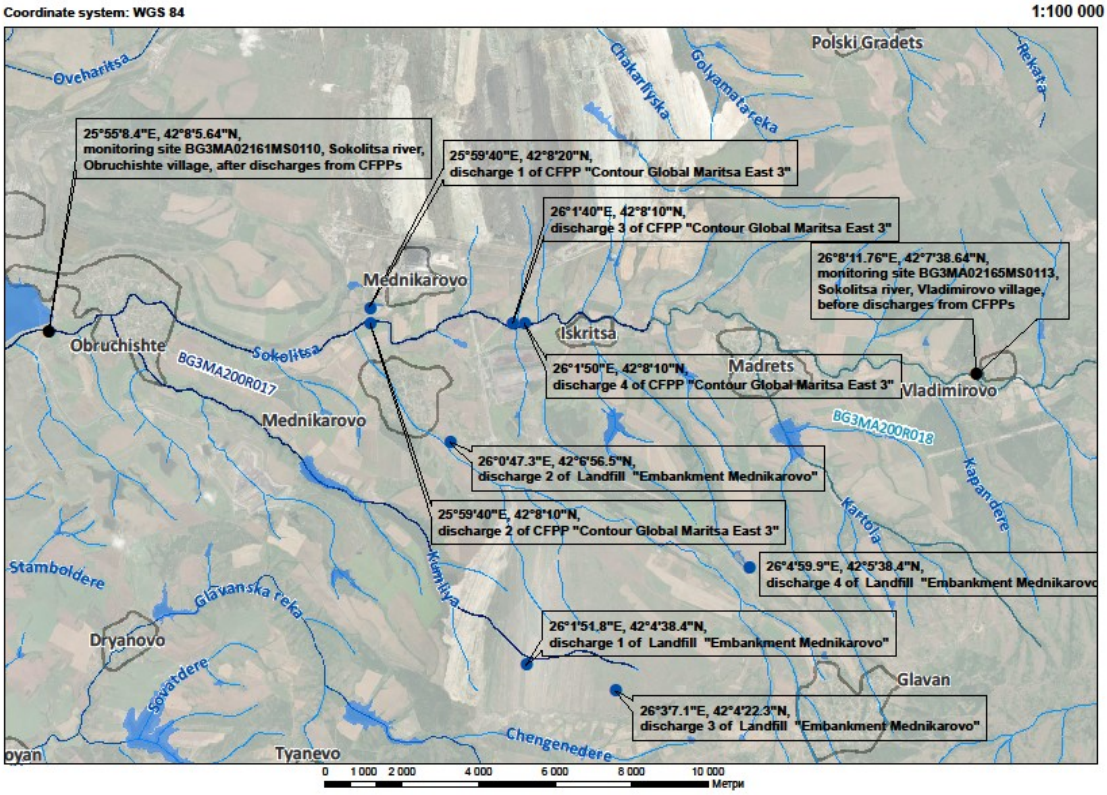

Fig. 3. Wastewater discharge points from facilities of CFPP "Contour Global Maritsa East 3", from Landfill of non-hazardous waste "Embankment Mednikarovo" and monitoring sites situated on Sokolitsa River.

Data collection and analysis

Data from conducted by West Aegean River Basin Directorate and East Aegean River Basin Directorate annual monitoring programmes of studied surface waters for ten-year period 2013-2022, as well from the investigative monitoring of Razmetanitsa River for August – December 2019 were selected and analyzed. Field sampling and analytical measurement activities were carried out by the regional laboratories of the Bulgarian Environmental Executive Agency in compliance with BDS EN ISO/IEC 17025:2018 standard.

The data for monitored biological quality elements (BQE) macrozoobenthos, phytobenthos and fish fauna were reviewed and analyzed. The analyzes for every BQE were done in accordance with the limits for good ecological status from the type-specific classification system for ecological status in Appendix 6 of Ordinance H-4/2012.

The basic physico-chemical parameters pH, dissolved oxygen (mg/l), biological oxygen demand (BOD5) (mg/l), chemical oxygen demand (COD) (mg/l), conductivity (µS/cm), calcium carbonate hardness (mg/l), inorganic nutrients – $N\text{-}NH_3$ (mg/l), $N\text{-}NO_2$ (mg/l), $N\text{-}NO_3$ (mg/l), N-total (mg/l), $P\text{-}PO_4$ (mg/l), P-total (mg/l), total suspended substances (TSS) were reviewed and analyzed. The analyses of the monitored basic physico-chemical parameters were done in accordance with the limits for good ecological status from the type-specific classification system in Appendix 6 of Ordinance H-4/2012. For some of above listed basic physico-chemical parameters like COD, calcium carbo-

nate hardness and TSS, which have not standards for good ecological status in Ordinance H-4/2012, the analyzes were done by comparison with data for the same parameters from unaffected by the CFPP pressure monitoring sites.

The specific pollutants manganese (µg/l), sulphates (mg/l), copper (µg/l), zinc (µg/l), iron (µg/l), cyanides (µg/l), phenols (µg/l), arsenic (µg/l), surfactants (mg/l), aluminum (µg/l), chromium (total) (µg/l), polychlorinated biphenyls (PCBs) (µg/l), polyaromatic hydrocarbons phenanthrene (µg/l) and pyrene (µg/l), uranium (µg/l), radium-226 (µg/l), total alpha-activity (Bq/l) and total beta-activity (Bq/l)) were reviewed and analyzed. The analyzes for the relevant monitored specific pollutants were done in accordance with the Environmental Quality Standards (EQS) in Appendix 7 of Ordinance H-4/2012. For some of above listed specific pollutants like sulphates (mg/l), chlorides (mg/l), phenols (µg/l) and surfactants (mg/l) which have not EQS in Ordinance N-4/2012, the analyzes were done by comparison with data for the same specific pollutants from unaffected by the CFPP pressure monitoring sites, located in surface water bodies from the same types.

The priority substances cadmium (µg/l), lead (µg/l), mercury (µg/l) and nickel (µg/l) were reviewed and analyzed. The analyzes for the monitored priority substances were done in accordance with the Environmental Quality Standards (EQS) for good chemical status in Appendix 2 of Ordinance on environmental quality standards for priority substances and some other pollutants.

Ecological status assessment of the observed affected surface water bodies BG4ST600R039 (Razmetanitsa River from the sources to the confluence with Dzherman River) and BG3MA200R017 (Sokolitsa River middle reaches to Rozov kladenets Dam) based on monitored biological quality elements, basic physico-chemical parameters and specific pollutants measured in the monitoring sites before and after the wastewater discharge points from CFPP facilities in Razmetanitsa and Sokolitsa watersheds was made.

Results

Values of the specific pollutant sulphates (average 133.4 mg/l) and the calcium carbonate hardness (average 105.89 mg/l) measured at the site BG4ST00662MS330, Razmetanitsa River before discharges of sludge dump "Black lake" of CFPP „Bobov dol" for the period August - December 2019 were several times lower than the values of the both parameters, sulphates (average 871 mg/l) and the basic parameter calcium carbonate hardness (average 878.5 mg/l), measured during the same period at the monitoring site BG4ST00662MS570, Razmetanitsa River after discharges of CFPP "Bobov dol" (Fig. 4).

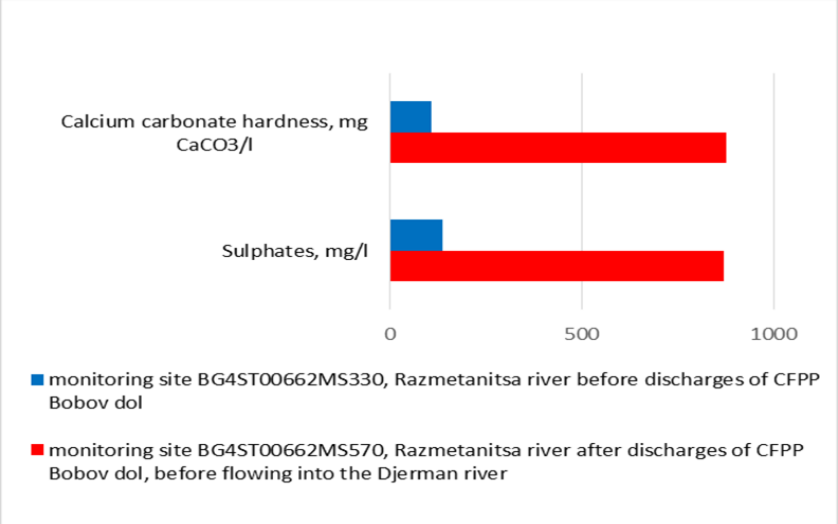

Fig. 4. Average values of monitored parameters measured in unaffected site and polluted sites located on the Razmetanitsa River (before and after discharges from CFPP Bobov dol) for the period August - December 2019.

Throughout the ten-year period 2013-2022 the values of the specific pollutants manganese, sulphates and calcium carbonate hardness in monitoring site BG4ST00662MS570, Razmetanitsa River after discharges of CFPP "Bobov dol" were registered to be several times greater than those measured at the monitoring site BG4ST00662MS330, Razmetanitsa River before discharges of sludge dump "Black lake"of CFPP „Bobov dol". The average value of the conductivity during the ten-year period 2013-2022 in monitoring site BG4ST00662MS570 was 1348 µS/cm. This value is almost two times higher than 750 µS/cm which defines limit of good ecological status for R13 river type (Fig. 5). The average concentration of the specific pollutant manganese in this site for the specified time period was 136.3 µg/l, which is more than two times and half higher than the value of 50 µg/l set in Ordinance N-4/2012 (Fig. 5 and Fig. 6). There were not monitoring data for the specific pollutant manganese and for the basic physico-chemical parameter conductivity in the site BG4ST00662MS330, Razmetanitsa River before discharges of sludge dump "Black lake of CFPP „Bobov dol" for the mentioned period.

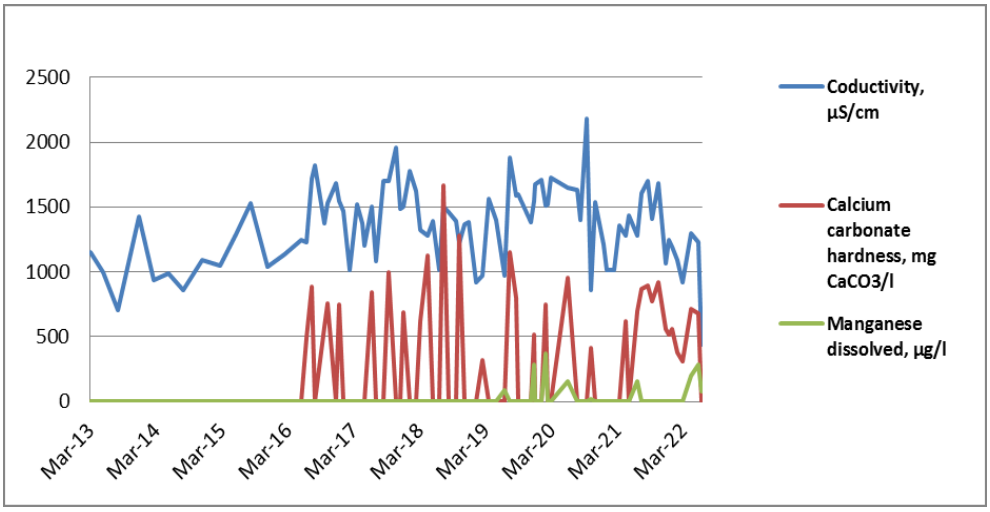

Fig. 5. Values of the conductivity, calcium-carbonate hardness and the specific pollutant manganese measured at the monitoring site BG4ST00662MS570, Razmetanitsa River after discharges of CFPP "Bobov dol" for a ten-year period (2013-2022).

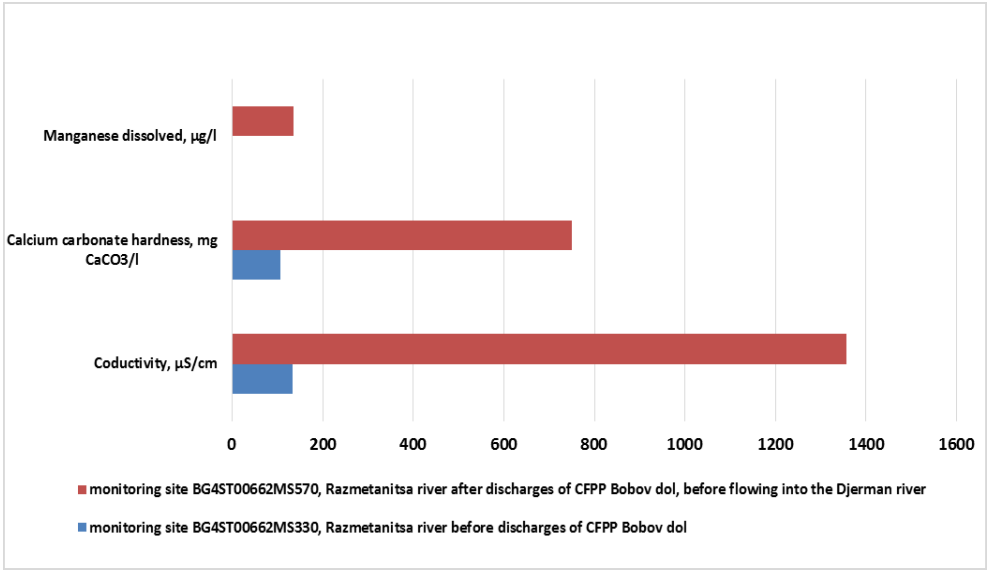

Fig.6. Average values of monitored parameters at unaffected site and polluted sites in Razmetanitsa River for a studied ten-year period (2013-2022).

The values of the specific pollutants sulphates and manganese and the basic physico-chemical parameters conductivity and calcium-carbonate hardness for whole observed ten-year period (2013-2022) at the monitoring site BG3MA02165MS0113, Sokolitsa River after discharges of CFPP facilities were several times higher than those measured at site BG4ST00662MS330, Sokolitsa River, Vladimirovo village, situated before wastewater discharges (Fig. 7-9).

Unfavourable ecological status assessment of the both observed surface water bodies BG4ST600R039 and BG3MA200R017 based on biological quality elements (BQEs) and physico-chemical parameters (was established (Table 1). In addition, exceedances of the EQS were also registered for the specific pollutants manganese, aluminum, arsenic, PCB 28, uranium), total alpha-activity and total beta-activity).

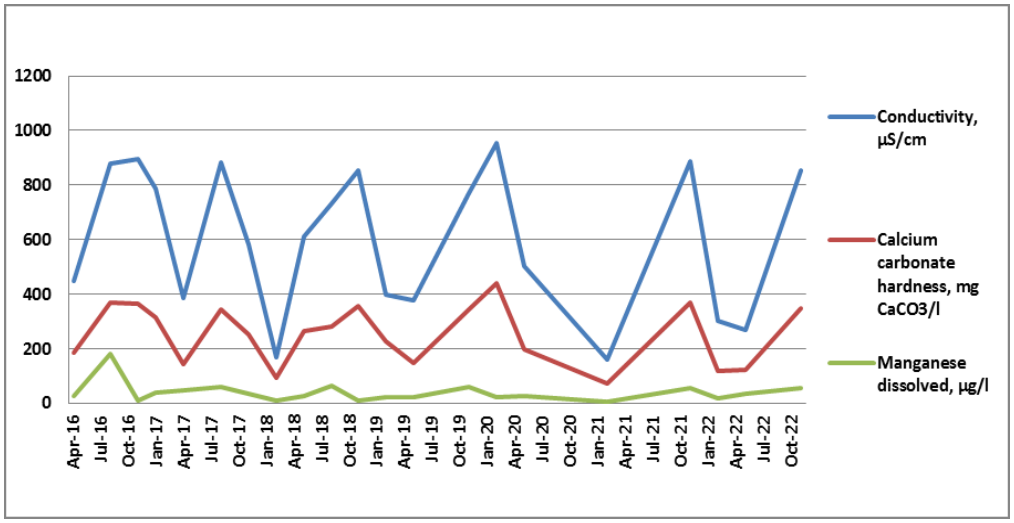

Fig. 7. Values of the basic physico-chemical parameters conductivity and calcium-carbonate hardness and the specific pollutant manganese at monitoring site BG3MA02165MS0113, Sokolitsa River near Vladimirovo village, before discharges of CFPP facilities for a ten-year period (2013-2022).

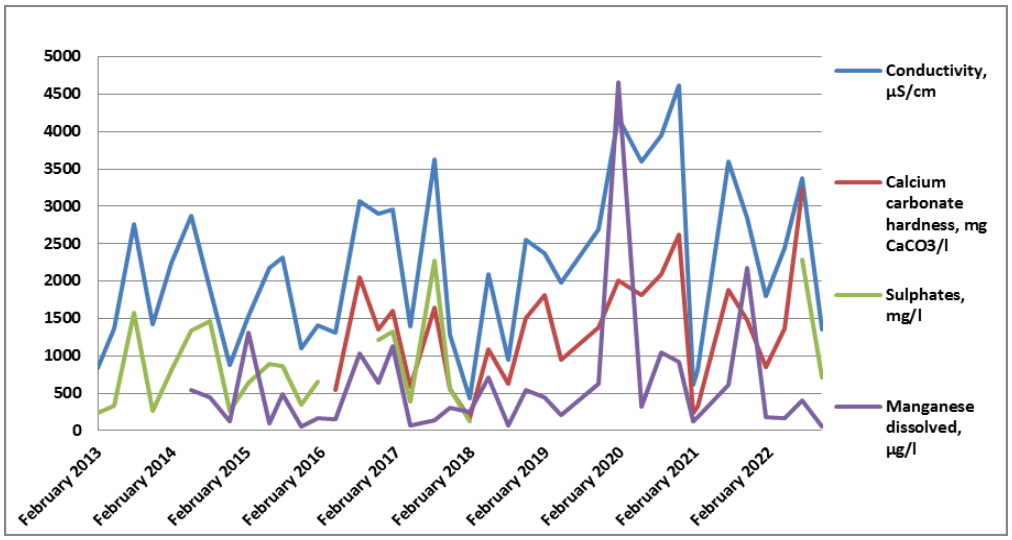

Fig. 8. Values of the basic physico-chemical parameters conductivity, and calcium-carbonate hardness and the specific pollutants manganese and sulphates at monitoring site BG3MA02161MS0110, Sokolitsa River near Obruchishte village, after discharges of CFPP facilities for a ten-year period (2013-2022)

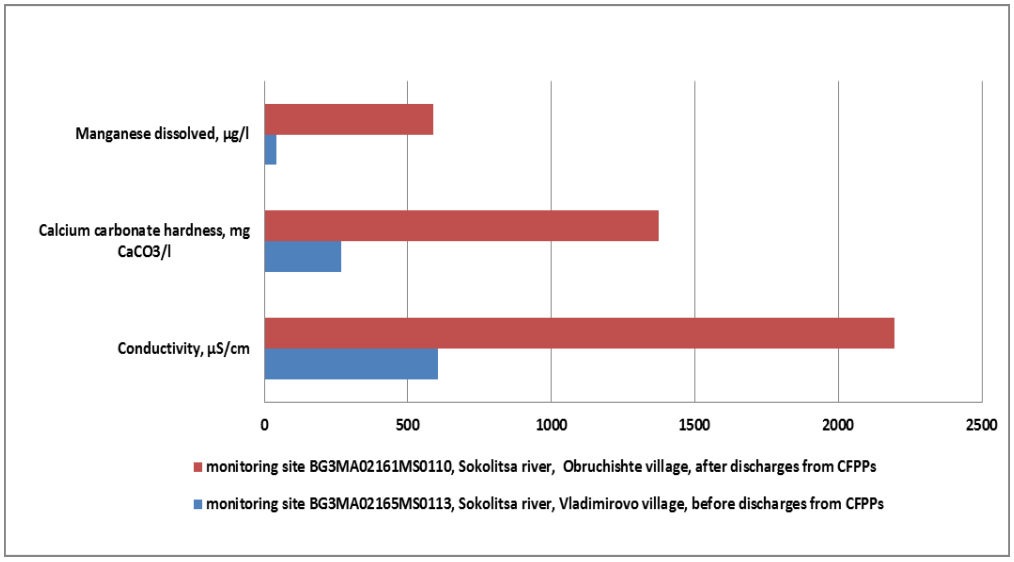

Fig 9. Average values of monitored parameters in unaffected and polluted sites in Sokolittsa River for ten-year period (2013-2022).

Table 1. Ecological status assessment of surface water bodies BG4ST600R039, Razmetanitsa River from the sources to the confluence with the Dzherman River, type R13, Struma catchment, West Aegean region and BG3MA200R017, Sokolitsa River middle reaches to Rozov kladenets dam, type R14, Maritsa catchment, East Aegean region.

Year of monitoring data	Ecological status of water body BG4ST600R039	Ecological status of water body BG3MA200R017
2013	Bad	Poor
2014	Bad	Poor
2015	Bad	Moderate
2016	Bad	Moderate
2017	Bad	Moderate
2018	Bad	Moderate
2019	Bad	Moderate
2020	Poor	Moderate
2021	Poor	Poor
2022	Bad	Poor

Discussion

Surface water impact caused by the activities of CFPPs is very serious due to its pervasive nature and negative influence on the aquatic ecosystems. According to EPA (2014) every year, CFPPs dump millions of tons of toxic pollutants into USA waterways. In Europe, the coal still accounts for more than 50% of fuel input in large combustion plants (LCPs) in five countries in EU including Bulgaria. LCPs (including CFPPs) are responsible for almost 40% of electricity generation capacity in the European Union (EU). They largely dependent on fossil fuels, leading to the emission of pollutants into the air, water and land, with harmful effects on ecosystems (European Environmental Agency (EEA), 2023). In Bulgaria, the majority of CFPPs and the largest of them are located in Maritsa River catchment and in Struma River catchment, in close proximity to coal mines which are also significant sources of pollution of soil, air and water (Ilinkin & Dimitrova, 2019).

Data showed that the total amount of the waste generated by activities of the CFPP „Bobov dol“and CFPP „Contour Global Maritsa East 3" for 2021 (3 289 310 tones) compared with the same amount total waste in 2015 (908 552 tones) has

increased more than three times (EEA, 2021). Part of this waste directly or diffusely falls into the adjacent waters, carrying a number of toxicants that deteriorate the quality of the waters, compromise habitats and suppress the vital activity of the aquatic flora and fauna.

Impact of the CFPP „Bobov dol" on Razmetanitsa River

During the observed period (2013-2022) in the monitoring sites of Razmetanitsa River, the specific pollutants manganese, arsenic, uranium and total beta-activity were registreted with exceedances compared to their EQS (according to Ordinance N-4/2012). Actually, the reference in IPPC-permit 45-N4-I0-A0/2019 of CFPP „Bobov dol" for discharges of wastewater from sludge dump „Black lake" in Razmetanitsa River showed that there are set individual emission limits for pH, TSS, petroleum products, chromium (total), copper, zinc, iron, BOD5, COD, increase in temperature of receiving river, residual chlorine, mercury, cadmium, thallium, arsenic, lead, nickel, dioxins and furans. According to this IPPC-permit, after 2022 discharge of the priority substances mercury, cadmium, dioxins and furans from the waste water of the "Black lake" of CFPP „Bobov dol" into the Razmetanitsa River is not allowed. In the same IPPC-permit 45-N4-I0-A0)/2019 there are not set individual emission limits for manganese, uranium and total beta-activity. In addition in the IPPC-permit 299-N/2019 of CFPP „Bobov dol" for Landfill of non-hazardous waste "Kamenik" for discharges of atmospheric/surface waters in Razmetanitsa River there are set individual emission limits for pH, TSS, chromium (total), copper, iron, zinc, petroleum products, phosphorus (total), ammonium nitrogen, manganese, arsenic, free cyanides, sulphates and chlorides. The monitoring data analyzed in the present study, showed very high values for calcium (characterized calcium carbonate hardness) and sulphates at the monitoring sites on Razmetanitsa River after the discharges from the CFPP „Bobov dol". But there is set individual emission limit only for sulphates in the IPPC-permit 299-N/2019 of CFPP „Bobov dol" for Landfill of non-hazardous waste "Kamenik". In the same time sulphates also do not have derived EQS in Bulgarian water legislation (Ordinance N-4/2012).

The registered exceedances of established EQS for the specific pollutants manganese and arsenic, and the high values of the basic physico-chemical parameters calcium and sulphates for the period 2013-2022 were reflected in the deteriorated ecological status of the surface water body BG4ST600R039, Razmetanitsa River from the sources to the confluence with the Dzherman River (Table 1). This confirmed the results of the research done by Greenpeace organization devoted to the negative impact of CFPP „Bobov dol"on the status of Razmetanitsa River (Brigden et al., 2019).

Registered in Razmetanitsa River specific pollutant PCB 28 (an organic pollutant from the group of polychlorinated biphenyls – PCB), with values above EQS (WARBD, Annual report, 2021), can be indicative of potential pollution with organic substances of the waters, as a result of the work of CFPP „Bobov dol". An assumption about a possible such type of impact on the status of Razmetanitsa River was also described in the research of Greenpeace (Brigden et al., 2019). In addition, Greenpeace research results showed presence of traces of other organic substances (pyrene – from the group of the polycyclic aromatic hydrocarbons (PAHs), diethyl phthalate, dibutyl phthalate, diisobutyl phthalate, bis(2-ethylhexyl) phthalate - phthalate esters and diethylene glycol diethyl ether in the discharged wastewater from Sludge dump "Black lake" in Razmetanitsa River. Thus, the above mentioned specific pollutants polychlorinated biphenyls and polycyclic aromatic hydrocarbons without set individual emission limits for discharged wastewaters in IPPC-permits of CFPP „Bobov dol"are not subject to self-monitoring by CFPP „Bobov dol" and of administrative control by the Bulgarian environmental authorities at fulfillment of conditions in IPPC-permit 45-N4-I0-A0)/2019 and IPPC-permit 299-N/2019.

Impact of CFPP "Contour Global Maritsa East 3" on Sokolitsa River

Specific pollutants manganese, aluminum, uranium, total alpha-activity and total beta-activity were most frequently registered with exceedances of their EQS (Ordinance N-4/2012) in Sokolitsa River monitoring sites during the observed period (2013-2022). Reference in the IPPC-permit 52-N0-I0-A2/2012 of CFPP "Contour Global Maritsa East 3" showed that there are not set individual emission limits for the mentioned specific pollutants. Individual emission limits for same specific pollutants were also not described in IPPC-permit 403-

N0/2010 of „Maritsa East Mines“ for discharged atmospheric/surface waters from Landfill for non-hazardous waste "Embankment Mednikarovo" in tributaries of Sokolitsa River. In this permition there are set individual emission limits only for pH, total suspended substances (TSS), iron, metals (total) and petroleum products. Previous survey about impact of the anthropogenic pressure from „Maritsa East Mines“ activities on the status of Sokolitsa River showed that discharged wastewaters had no significant impact on water quality of this river as a source for irrigation (Dermendzhieva et al., 2018).

The monitoring data for Sokolitsa River during the observed period (2013-2022) also revealed very high values for calcium (calcium carbonate hardness) and sulphates, as those reported for Razmetanitsa River. There are not set individual emission limits in IPPC-permits of CFPP "Contour Global Maritsa East 3" and „Maritsa East Mines“ for these substances, also they are not subject to self-monitoring by holders of above mentioned IPPC-permits and to administrative control by the Bulgarian environmental authorities.

Results revealed in the both case studies exceedances of the specific pollutants (uranium, total alpha-activity and total beta activity) which are related to radioactivity. The origin of these exceeded values and their potential relationship to the activity of CFPPs in the observed river watersheds has not been established yet. The European Commission is aware that CFPPs and radioactive ash from these plants could be of concern from a radiation protection point of view (European Parliament, Parliamentary question - E-003567/2022). Directive 2013/59/Euratom addresses human activities which involve the presence of natural radiation sources and offers a legal framework for the regulatory control of these activities and provisions for the protection of workers and the public exposed to these radiation sources. It explicitly lists CFPPs as one of the industrial sectors to be considered to be subject to regulatory control by Member States (Council Directive 2013/59/Euratom). According to EPA (2023) the process of burning coal at CFPPs creates wastes that contain small amounts of naturally-occurring radioactive material. This fact should not be neglected, but put under strict control by the state institutions in each country where such CFPP are used.

This study covered a limited number of quality parameters, specific pollutant and priority substances. At the same time, the specific composition of the mined and used coal in the surveyed CFPPs showed significant presence of large number of other polluting substances like boron, bismuth, bromine, chlorine, cesium, fluorine, iodine, lithium, molybdenum, strontium and vanadium in them and in produced after coal combustion ash, deposited in sludge dumps. The listed polluting substances can easily pass into surface waters and pollute them (Vasilev & Vasileva, 2005). This process of passage and contamination of surface water with other pollutants was confirmed by Brigden et al. (2019). Authors found high concentrations of the metals and metalloids aluminum, boron, barium, rubidium, molybdenum and vanadium in the samples taken from Razmetanitza, down of discharges from sludge dump „Black lake“. It should be emphasized that these substances have not been included in the official monitoring carried out by the regional inspectorate of environment and waters and basin directorates until now nor are set individual emission limits for them in the IPPC-permits of CFPPs and their activities, both in two studied rivers – Razmetanitsa and Sokolitsa.

Negative influence of the studied pollutants on the water ecosystems

Numerous aquatic ecosystems have been studied with respect to the habitat modifications with the focus primarily being on inorganic contaminants associated with CCR (coal combustion residuals). Concentrations of several trace elements (primarily cadmium, chromium, copper, lead and selenium) have been particularly well characterized in several CCR-impacted systems because of the abundance of these elements in waste waters from CFPP and/or concerns associated with the known toxicological actions of these elements. Some of discharged in receiving waters pollutants are rapidly accumulated to high concentrations by the aquatic organisms. In some vertebrates and invertebrates, coal combustion pollutants exposure led to numerous histopathological, behavioral, and physiological (reproductive, energetic, and endocrinological) effects (Rowe et al., 2002). Arsenic, discharged from CFPPs, accumulates in aquatic plants and sediments and it is difficult to remove from an aquatic ecosystem.

This pollutant reduces algae and biomass growth in freshwaters and shortens life of aquatic invertebrates and certain amphibians. Arsenic and sulphates which constantly appeared with very high values in Razmetanitsa River and Sokolitsa River, also affect the material cycles of carbon, nitrogen and phosphorus. This increases the nutrient loads in water bodies and thus influence on the growth of plants and algae as well as on the food supply for aquatic organisms. The result is a lack of oxygen in the water, which promotes the further release of phosphate from the sediment – a vicious cycle. Sulfate and its degradation products – especially sulfide – can also have a toxic effect on aquatic life (Zak et al., 2021) Contaminated with sulphates waters of Razmetanitsa River have already caused secondary pollution of the river-related groundwaters located in the alluvial deposits - captured spring „Tsarichina" which is used for drinking water supply of Balanovo village, Dupnitsa municipality, Kyustendil region (WARBD, Annual reports 2013-2022).

Water hardness i.e., a measure of calcium (Ca^{2+}), magnesium (Mg^{2+}) and/or iron (Fe^{2+}) in water, is crucial for the growth, reproduction and embryo-development of fish (Krishnakumar et al., 2020). The water hardness has indirect impact on the blood calcium levels and osmoregulation in aquatic organisms. At the other hand, the hardness of water influences on bioaccumulation and toxicity of metals. Generally, higher hardness results in lower toxicity of metals in water (Established EQS for specific pollutants zinc and copper in Ordinance H-4/2012 and EQS for priority substances cadmium, lead and nickel in Directive 2013/39/EC). Exceeded levels of aluminum can affect some species' ability to regulate ions, like salts, and inhibit respiratory functions, like breathing. Aluminum can be accumulated on the surface of a fish's gill, leading to respiratory dysfunction, and possibly death (US EPA, 2018).

The high concentrations of metals such as manganese, iron and aluminum from point-source metal pollution is a major cause of the loss of macroinvertebrate diversity in small streams and rivers (Doi et al., 2007). In confirmation of this finding worsened ecological status of biological quality element macrozoobenthos, was ascertained in both case studies (Table 1).

Conclusions

Our study found that during the observed period (2013-2022) the registered very high values of the basic physico-chemical parameters calcium (calcium carbonate hardness), sulphates and specific pollutant manganese in Razmetanitsa River and Sokolitsa River are the result of activities of CFPP „Bobov dol" and CFPP "Contour Global Maritsa East 3" which is directly connected with the deteriorated ecological status of the both rivers. In the Bulgarian water legislation, there are no established quality standards for sulphates, chlorides, boron, barium, rubidium, molybdenum, vanadium, selenium in the inland surface waters. This causes serious difficulties in the evaluation of their influence on the ecological status of the rivers, polluted from CFPPs waste-water discharges. The monitoring carried out by the state environmental protection authorities and from holders of IPPC-permits has to be done through sensitive analytical methods with low and appropriate limits of determination and high accuracy of quantity and quality measurements. By this approach will be obtain reliable data of the discharged amounts of concentrations from the number and type of all identified significant pollutants which negatively influence on the status of the receiving surface waters. The impact of the pollutants on the aquatic habitats and biota should be assessed to save water quality and integrity of aquatic ecosystems.

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