Pollution of Varna Lake and possibilities of using the pollutants as resources

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Abstract. Varna Lake is of great social and economic importance for the city of Varna and the entire region. The urbanisation of the areas surrounding the Varna-Beloslav Lake complex and the accelerated industrialisation around the coastline of Varna Bay have significant anthropogenic pressure on the aquatic ecosystem. An essential aspect is that industrial development, maritime transport and urbanisation are substantial sources of large-scale inorganic and organic pollution with all the resulting negative consequences. Recent measurements show that the surface sediments, which are a source of nutrients for the water body of Varna Lake, are contaminated with heavy metals and oil products. In this paper, we present a quantitative assessment of the degree of contamination with heavy metals (Hg, As, Fe, Cu, Pb) and petroleum products in the upper sediments of Varna Lake and then discuss opportunities for using some of these pollutants as a resource. The exploitation of these resources would bring significant benefits for improving the ecological status of Varna Lake.

1 Introduction

Varna Lake is located within the borders of the northern Bulgarian Black Sea coast. Until the digging of the first canal between the Varna and Beloslav Lakes in 1923, these lakes were a single lake basin. According to its genesis, the lake belongs to the seaside lakes [1]. Two artificially excavated navigation channels connect the lake to Varna Bay. Lambev et al. carried out measurements in Varna Lake and determined an area of 15.7 km2, a maximum depth of 21.3 m, a maximum length of 10.5 km and a maximum width of 2.5 km [2].

The Varna-Beloslav Lake complex has significant social and economic importance for the surrounding areas. At the same time, the anthropogenic influence on the lakes is increasing with the acceleration of urbanisation and industrialisation of Varna Bay coastal areas. Specifically, industrial development, maritime transport and urbanisation are identified as the primary sources of heavy inorganic and organic pollution. This leads to the deterioration of the ecological condition of the water body of the Varna-Beloslav Lake complex, which refers to the eutrophic type of lakes. During the circulation of substances in these lakes, part of the produced organic substances is preserved without being mineralised,

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accumulating mainly in the bottom sediments. Besides organic substances, heavy metals (mercury (Hg), arsenic (As), iron (Fe), copper (Cu), lead (Pb)) and petroleum products accumulate in the sediments.

In this report, we present a quantitative evaluation of the degree of contamination of the sediments of Varna Lake with the above-mentioned heavy metals and petroleum products. Conceptual ideas for cleaning the lake sediments are discussed, as well as methods for cleaning which consider these pollutants as a resource. Such a cleaning, in turn, will support the sustainable management of water resources in the area.

2 Methods

From October 2021 to February 2022, 140 bottom samples were taken from the surface sediments of Varna Lake. Each sample was taken 40 cm below the bottom level. Sampling was carried out by qualified diving teams in two pre-selected target areas (Zone 1 and Zone 2), according to a predetermined measurement grid with a distance between sampling sites of 200 m [3]. Zone 1 covers the eastern parts of Varna Lake and the two navigation channels connecting it to Varna Bay. Zone 2 is located in the central part of Varna Lake, near the village of Kazashko Figure 1.

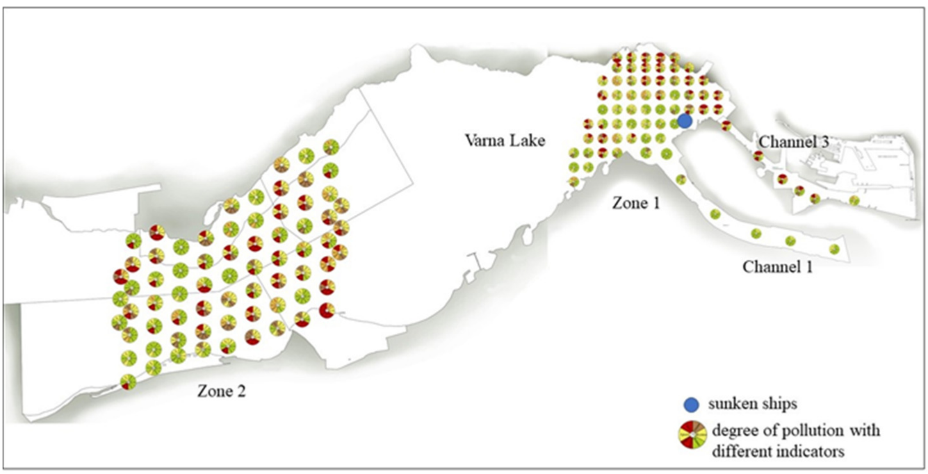

Fig. 1. Extent of the researched area, according to the Hydro Map with additions.

The bottom sediment samples were taken at a maximum working depth of 19.5 m below the water surface, with visibility of 0 ÷ 1.40 m and a water temperature of 12 °C. All 140 samples were subjected to chemical analysis to assess contamination levels with heavy metals and petroleum products. The chemical analysis was carried out by Eco-Consult-Engineering OOD - an accredited laboratory in Burgas. This analysis aims to evaluate metal tracers such as mercury (Hg), arsenic (As), iron (Fe), copper (Cu), lead (Pb) and petroleum products. Identifying the metal indicators mentioned above: Iron/Fe, Lead/Pb, Arsenic/As, Copper/Cu, and Mercury/Hg was made according to the procedures described in the Bulgarian national standard -- test method BDS EN 16170:2016 (https://bds-bg.org/bg/project/show/bds:proj:99534). The identification of petroleum products in the probes was carried out according to the procedures defined in the Bulgarian national standard BDS EN ISO 16703:2011 (https://bds-bg.org/bg/project/show/iso:proj:39937). In these analyses, we considered the commonly accepted unit of measurement for the indicators -- $mg.kg^{-1}$.

The reference values used in the subsequent assessment of contamination levels follow the International Atomic Energy Agency (Reference sheet IAEA-158/31.08.2008 and Reference sheet IAEA – 459/10.06.2017) (Reference sheet IAEA-158/31.08.2008 and Reference sheet IAEA – 459/10.06.2017). The reference sheets have no aggregate reference values for petroleum products but are broken down by type. Therefore, when preparing the legend for petroleum products, the reference value was taken based on the average value of the laboratory samples, and the rest were defined as contaminated and uncontaminated areas [3].

3 Results

Varna Lake is defined as highly modified. As a result of human activity, its physical characteristics have undergone significant change. The quality of the aquatic environment is determined by the ecological potential of the lake itself. We can consider three categories of ecological potential - good, medium, low and bad, depending on the level of effort invested in environment protection. The environmental assessment of the waters of Varna Lake is within the limits of low potential, with minor exceptions near the lake-bay contact zone, where it is medium. In recent years, due to a drop in production in the chemical complex in Devnya, the TPP (Thermal power plant) Varna and the Beloslav glass production factory, there has been a decline in the influence of industrial activity in the area. The maintenance of the state of the lake system in "low-poor quality" of ecological potential is due to the loading and unloading activities of the ports, the waters from the Provadiyska River, the reduced capacity of the treatment plants, the increasing urban population, etc. In general, the ecological potential of the lake varies from good to bad, with 52% having an average, 27% good and 19% bad potential [4]. The polluted sediments and the dredged material depot located in the water area of the lake have a significant impact on its ecological condition.

The surface sediments are an essential source of nutrients for the water body of Varna Lake. The nutrients released from the sediments exceed the total external load and are sufficient to support hyper eutrophication. Even with significant reductions in point source inflow, benthic streams will continue to support high primary production and subsequent organic loading. This, in turn, will cause nutrient recycling leading to enhanced primary production. This suggests there needs to be more opportunity for the Varna-Beloslav Lake complex to meet WFD requirements for good condition [5].

At present, the hydrochemical characteristics of Varna Lake are determined by its connection with Beloslav Lake and Varna Bay. This is because Beloslav Lake receives polluted industrial and domestic wastewater, through which heavy metals, petroleum products and detergents enter the lake. The lead, copper, arsenic and cadmium concentrations are higher than in the bay [6].

After an analysis of the average contamination of all samples from the two areas of interest, it was observed that the most significant accumulation of iron, lead and copper is in Zone 1, and the highest pollution in Zone 2 is due to arsenic, mercury and petroleum products Figure 2. The accumulation of these heavy metals and petroleum products in the sediments of Varna Lake is due to the solid industrial pressure, urbanisation and shipping [3]. After a comparison of the average values of pollution in the two zones, it was observed that the indicators - mercury, copper and petroleum products prevail over the others.

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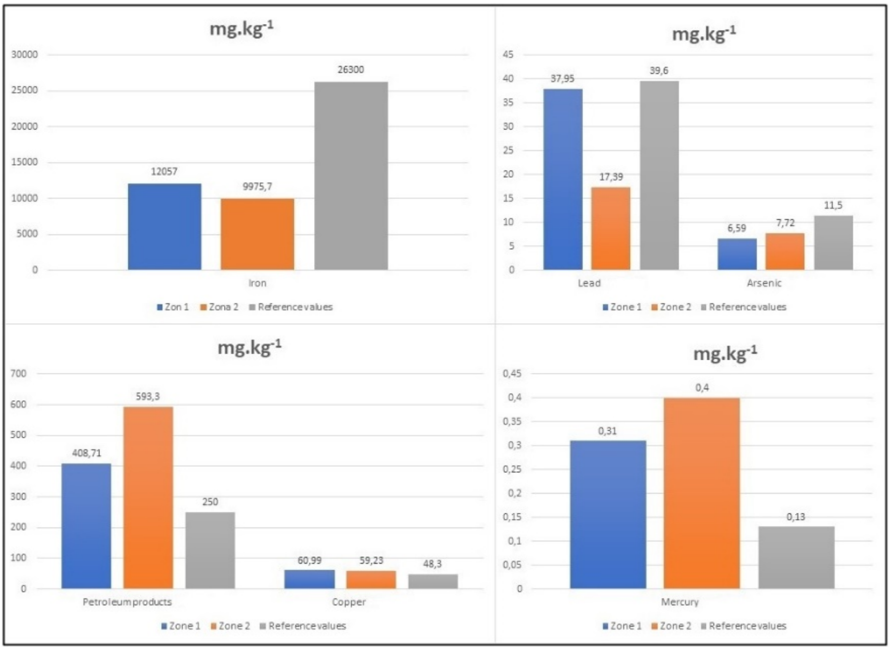

Fig. 2. Average pollution values in Zone 1 and Zone 2.

Finer-textured sediments with higher organic content accumulate higher concentrations of heavy metals than coarse sediments. This depends on the specific hydrodynamic conditions influencing the distribution of fine particles, such as silt and clay. A large part of the heavy metals are retained in the slag of the treatment plants but also easily reach drinking water [7]. In marine areas, such as Varna Lake, which have a low deposition energy, the accumulation of fine particles and pollutants is facilitated, while in those characterised by a high deposition energy (waves, currents), coarse particles (sand) prevail. The speed of the currents in Varna Lake is relatively low, and fine sediments are deposited, in which the pollutants are retained and accumulated.

It has been established that there is a constant intensive water exchange between Varna Lake and Varna Bay, where seawater mainly intrudes through Channel 1 in the west direction, and lake waters are directed to the bay through the old channel. This direction of the lake-bay water exchange may account for the more significant pollution in the Old Channel, as more heavily polluted lake waters pass through it in the direction of the bay. Another reason for the difference in the contamination could be that in Channel 1, periodic dredging of the bottom is carried out to provide a navigable depth Figures 3 and 4. Given the direction of movement of the lake waters and the location of the dredged material dump, there is a possibility that fine sediments and their pollutants are transported to the Old Channel [3].

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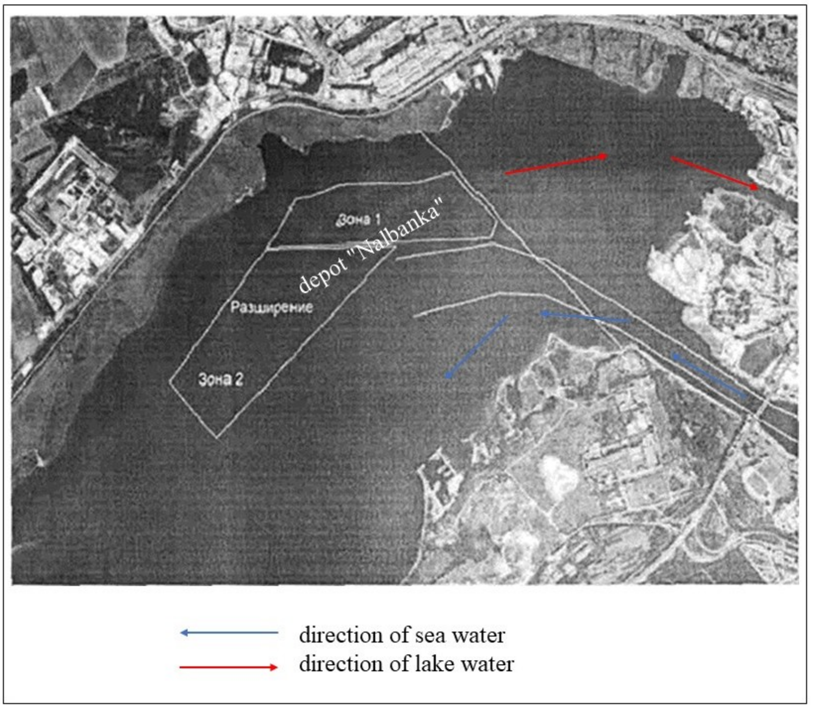

Fig. 3. Location of a landfill for dredged sediments in Varna Lake [8].

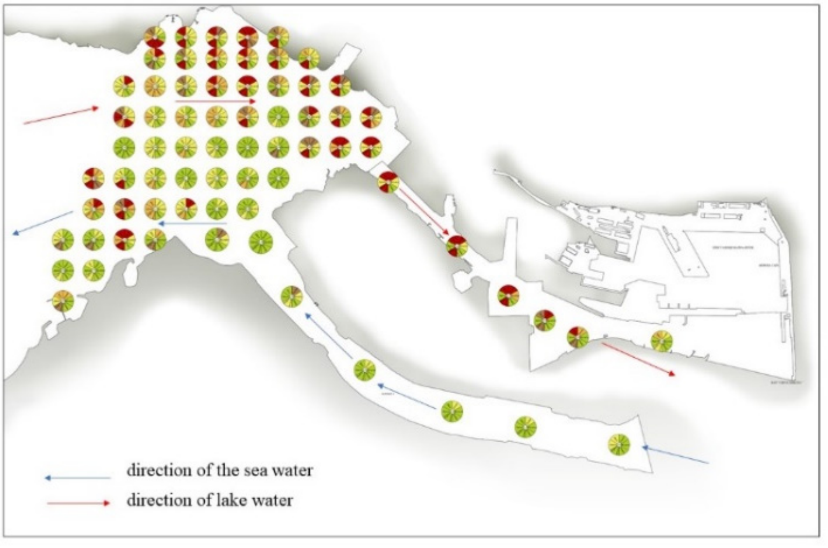

Fig. 4. Pollution in Zone 1 and direction of water exchange (lake-bay), according to the Hydro Map, with additions.

All accumulated pollutants in the sediments of Varna Lake are continuously released into the water body and contribute to maintaining its poor ecological condition. This, in turn, directly impacts the normal functioning of the ecosystem and biodiversity and is a prerequisite for the accumulation of pollutants in the body of aquatic inhabitants and the subsequent impact on human health. Restoring the self-purification function of the water bodies will improve their ecological status, contributing to their sustainable management.

In addition to pollution with heavy metals, petroleum products and eutrophication, there are remains of sunken ships in the Varna Lake area, which, in addition to pollutants, can hinder navigation Figure 5. It is necessary to survey and document all ship remains and consider measures for their removal and subsequent recycling. The use of ship remains for raw material and recycled iron will help clean the lake's water body.

Fig. 5. Remains of sunken ships in the Varna Lake area. (a) Iron fragments visible above the water surface. (b) Sinken fragments below the surface.

In Varna Lake, near the Kazashko village, the presence of estuarine healing mud has been established. It has been formed for thousands of years and is used for treatment in balneology. After 1978, Vladeva et al. conducted annual surveys of the deposit and found changes in the pH of the healing mud and the presence of mercury in some areas [9]. By bringing the lake to a good ecological condition and protecting the site from pollution, there will be favourable conditions for developing balneological tourism. This, in turn, will lead to new jobs being created for the population.

Various methods can be used to prevent the negative consequences on Varna Lake and bring it into a good ecological state, which will favour the blue and circular economy by turning waste (pollutants) into a resource.

Different methods are used for phytoremediation and bioremediation of sediments contaminated with heavy metals, petroleum products and organic substances. They use plant species, zeolites, microorganisms, etc., to remove contaminants. The removal of the dredged sediment dump will have a beneficial effect on the ecological status of the lake. The sediments can be subjected to phyto- and bioremediation and used as a bulk material to raise the level of lake shores Figure 6. The improvement of the ecological condition of the water body of Varna Lake will have a favourable impact on the development of various forms of alternative tourism (fishing, educational, spa, etc.).

Fig. 6. Bulk works along the shore of Varna Lake [10]

Biomass can be used for heating, electricity production and transport of biofuels. It is a natural, completely self-renewable and essential alternative source of energy. Biomass is obtained from different types of organic matter: energy plants, forests, agricultural and urban waste, including wood and household waste, and others. In Bulgaria, there is a great potential for biomass suitable for biogas production [11, 12].

The common reed (*Phragmites australis*) is a characteristic herbaceous plant along the shores of the entire lake complex Figure 7. Its presence contributes to water purification and sediments on the coasts. On the one hand, it can be used for phytoremediation by expanding its areas; on the other hand, the biomass (plant waste) can be used to produce biofuels and energy. Using biomass for energy purposes practically does not pollute the environment, and therefore it is considered a source of ecologically clean or "green" energy. In October 2022, one of the chemical industry enterprises in the Solvay Sodi region developed and presented a project to construct an installation for the thermal treatment of alternative fuels from non-hazardous waste and biomass. In this way, the enterprise will ensure long-term competitiveness and sustainability, improve regional air quality, help in waste management, etc. After building the plant, the company could use the biomass from the reed areas.

Fig. 7. Phragmites australis

Fig. 8. Sewage drainage channel of the Padina tailings pond

Wastewater from the chemical industry complicates the ecological condition of the water body. It is necessary for enterprises to be stimulated and supported in investments related to the use of recycled wastewater in the production process. This will reduce pollutants introduced into the lake and water costs, as businesses will repeatedly recycle and reuse the processed water in production Figure 8.

Fig. 9. State of the water body

The presence of elements such as nitrogen and phosphorus in large quantities causes eutrophication of the water body, destroying aquatic organisms Figure 9. Phosphorus is an exhaustible natural resource. Its presence in the water body and sediments should be reassessed because its extraction can provide a recycling solution. This calls for cross-sectoral cooperation and cost-effective ways to recover and reuse phosphorus and other resources from waters and sediments [13].

It has been proven that the cultivation and use of algae as a source of biofuels has numerous benefits for the environment and enables the development of a circular and blue economy. Algae is a versatile feedstock that can be used to refine various end products such as biodiesel, bioethanol, biomethane and biohydrogen. There are opportunities to build a waste-free technology for the simultaneous production of electricity and biofuels. The produced biofuel does not contain sulphur and is non-toxic, biodegradable and relatively harmless to the environment. Algae cultivation requires land unsuitable for agriculture, carbon dioxide, solar radiation, and polluted water, which the algae use as food. The nitrates, ammonia and phosphates that pollute the water serve as nutrients for the algae. In addition, algae are great biofixers – one metric ton of biomass absorbs 1.6 t of CO_2, producing 1.2 t of oxygen [14]. They take CO_2 from the atmosphere to use as a form of energy for themselves. Linking algae cultivation for biodiesel with the production of wastewater and the release of CO_2 is a perfect opportunity to protect lake waters, improve air quality in the area and create new jobs.

Important for the Bulgarian maritime economy are sectors such as maritime tourism, aquaculture, maritime transport, port activities, shipbuilding, ship repair, etc. These sectors are the basis of the "Blue Economy" of the Black Sea regions of Bulgaria and depend on the quality of natural ecosystems and coastal and marine resources. That is why it is essential to maintain a good ecological condition of Lake Varna for the normal functioning and development of the circular and blue economy and the sustainable management of water resources.

4 Conclusions

As a result of the conducted research on sediments in Varna Lake, elevated values of mercury (Hg), arsenic (As), iron (Fe), copper (Cu), lead (Pb) and petroleum products were found. Their accumulation in the sediments of Varna Lake is due to the solid industrial pressure, urbanisation, shipping, polluted waters from inflowing rivers, reduced capacity of treatment plants, etc. When comparing the average pollution values in the two studied areas, it was found that mercury, copper and petroleum products prevail over the others. The ecological assessment of the waters of Varna Lake is within the limits of low potential, with minor exceptions near the lake-bay contact zone, where it is medium. Of great importance for their sustainable management is their introduction into a good ecological condition and restoration of self-purifying functions.

Phytoremediation, bioremediation of sediments contaminated with various heavy metals, petroleum products and organic substances can be mentioned as good practices for cleaning the sediments and the water body; wastewater recycling; cultivation and use of algae as a source of biofuels; extraction of phosphorus from polluted areas and its reuse, etc. Various methods can be used to prevent the negative consequences on Varna Lake and bring it into a good ecological state, which will favour the blue and circular economy and sustainable management of water resources by turning waste (pollutants) into a resource.

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