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Assessment of a Metallurgical Plant Impact on the Sea of Azov

Abstract: Ferrous metallurgy enterprises have a negative impact on the air, soil, and water environment. The activities of metallurgy enterprises include a wide range of production processes (from the extraction of metals from ores to obtaining finished products) and is associated with the formation of a large amount of waste. Industrial wastewater discharge is the main source of aquatic area pollution. An assessment of the impact of wastewater discharged from the Azovstal Iron & Steel Works metallurgical plant on the state of the coastal waters of the Sea of Azov near Mariupol (Ukraine) is presented in the article. The assessment was carried out in accordance with the current Ukrainian legislation and the adopted methodology for water state assessment. The assessment was based on the available monitoring data of sea water in the area of wastewater discharges in the period 2016–2020. The assessment was carried out using the aggregated numerical indices, as well as taking into account the "limiting criterion principle". Such a methodological approach allowed for a comprehensive assessment of the sea water quality class as well as its sanitary and ecological condition. The results of the assessment allowed us to ascertain the negative impact of industrial wastewater from the metallurgical plant on the coastal zone of the Azov Sea, which made it unsuitable for communal and recreational purposes.

Keywords: metallurgical industry, the Sea of Azov, wastewaters, numerical aggregated indices

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1. Introduction

Currently, problems of environmental security have arisen as a result of human activities and are beginning to determine the prospects for socio-economic development. It has been shown that greater anthropogenic pressure of economic activity on the environment is provoked by higher levels of production and consumption. Progressive environmental pollution leads to the degradation of natural ecosystems, resource depletion and adversely affects human health [1, 2]. As a result, many countries are experiencing an acute shortage of fresh water, mostly resulting from the increasing water demand for municipal and industrial purposes [3–7].

Industrial enterprises are the biggest water consumers and at the same time the most dangerous source of wastewaters discharged into the aquatic environment. Particular attention should be paid to the activities of heavy industries (metallurgy, mining, and chemical) [8]. For example, coke chemical industry production is a main component of iron ore smelting process. Its activities provoke emissions of particulate matter, volatile organic compounds, heavy metals, Ca^{2+} and SO_4^{2-} ions into the environment. Additionally, the metallurgical industry is closely related with the energy sector and is one of the largest industrial CO_2 emitters [9, 10]. These enterprises are major sources of extremely hazardous pollution of the air, soil, and water environments by phenols and acids, coarse impurities and cyanides, arsenic, cresol etc. discharged with industrial wastewaters and other types of wastes [11–19]. The presence of such harmful compounds in the environment adversely affects the state and ability for all ecosystems to function properly, but it is particularly harmful to human health. Their impact level on the environment is determined by the following factors: production characteristics; technological process efficiency; type and condition of the equipment used; raw materials quality; requirements for final production as well as water and waste management [20].

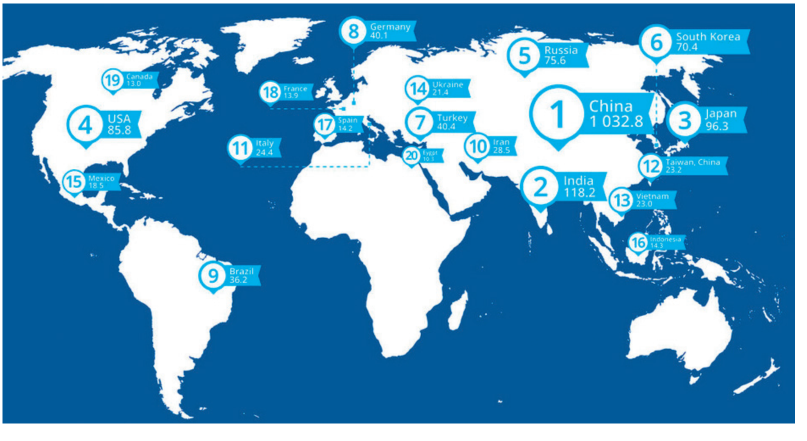

Fig. 1. Top 20 steel-producing countries 2021 (million tonnes)

Source: [21]

Ukraine is ranked the 14th in world steel production according to the World Steel Association rankings in 2021 (Fig. 1) [21, 22].

Figure 2 presents amount of crude steel production in the world and in Ukraine in the period from 2011 to 2021.

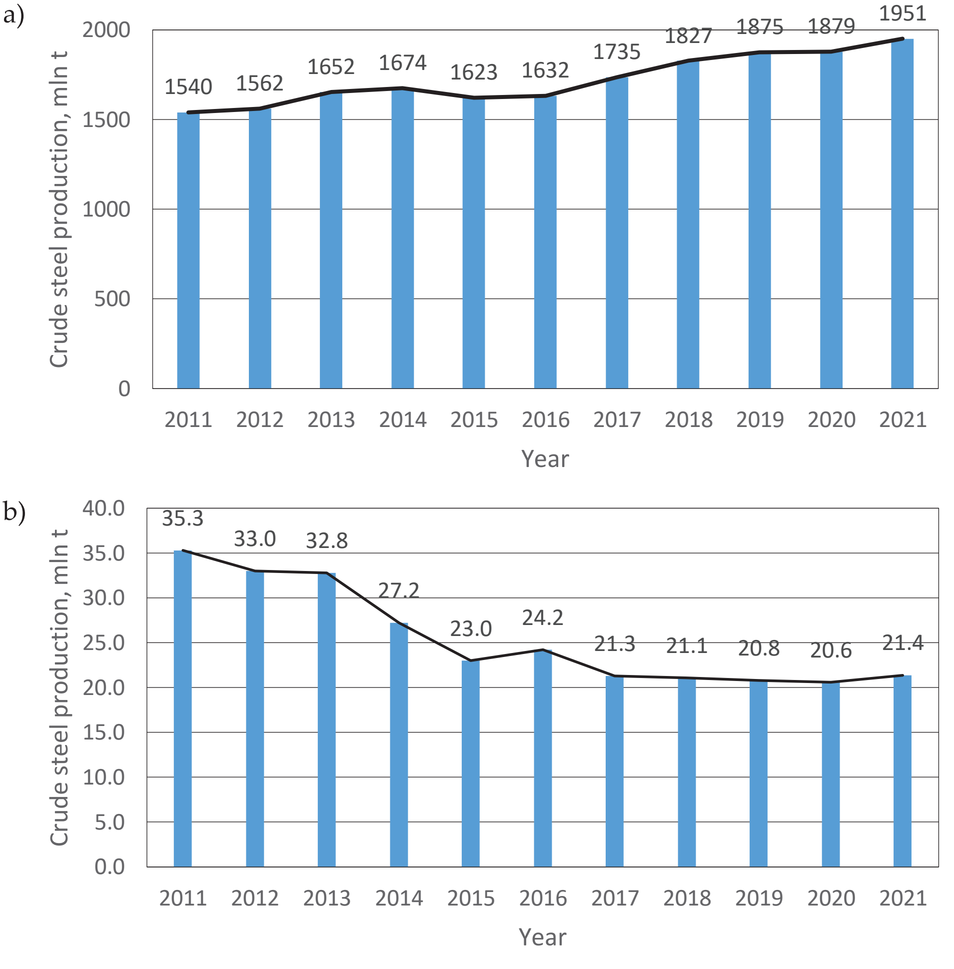

Fig. 2. Crude steel production in the world (a) and in Ukraine (b) in the period from 2011 to 2021

Source: based on [22–32]

Crude steel production in Ukraine in 2021 amounted to 21.4 million tonnes. The general trend of crude steel production in 2011–2021 was a downward one and decreased by almost 1.5 times, while the world steel production during the same period increased from 1,518 to 1,951 million tonnes. This fact can be explained by the political and economic situation in Ukraine.

Metallurgical industry embraces various water-consuming technological processes (mining and ore-dressing, production of iron and steel, refining of metals, metal forming, etc.). The ferrous metallurgy of Ukraine consumes up to 15% of the total amount of water consumed by the whole industrial sector. The unit water consumption is within the range of 4.79–12.20 m^3 per 1 tonne of steel [33]. In Europe, the average water consumption in such plants is significantly lower, ranging 1.6–3.3 m^3 per 1 tonne of steel [34]. Such high water demand brings to the production of great amount of wastewater.

According to statistical data [34, 35] the water consumption by the metallurgical industry of Ukraine is gradually decreasing (from about 630 million tonnes of fresh water in 2010 to about 460 million tonnes in 2020), which is connected with both the reduction of metallurgy production and the introduction of closed water cycles and resource-saving technologies [33].

Annual water consumption and wastewater discharge generated by Ukrainian enterprises of heavy industry is presented in Table 1 according to [20] on the basis of the available data.

Table 1. Water consumption and wastewater production in heavy industry sector in Ukraine

Industry	Water consumption [million m^3/year]	Wastewater [million m^3/year]
Metallurgy	1,535.0	1,292.0
Mining	114.0	112.0
Coke-chemical	41.8	15.5
Tube rolling	31.0	24.2
Refractories	6.0	9.7
Ferro alloys	5.7	0.9
Engineering	1.3	0.7

Source: [20]

Figure 3 shows the annual ratio of wastewater amount and water consumption by heavy industry in Ukraine. The highest ratio value is to be found in the metallurgy, mining and refractories industries.

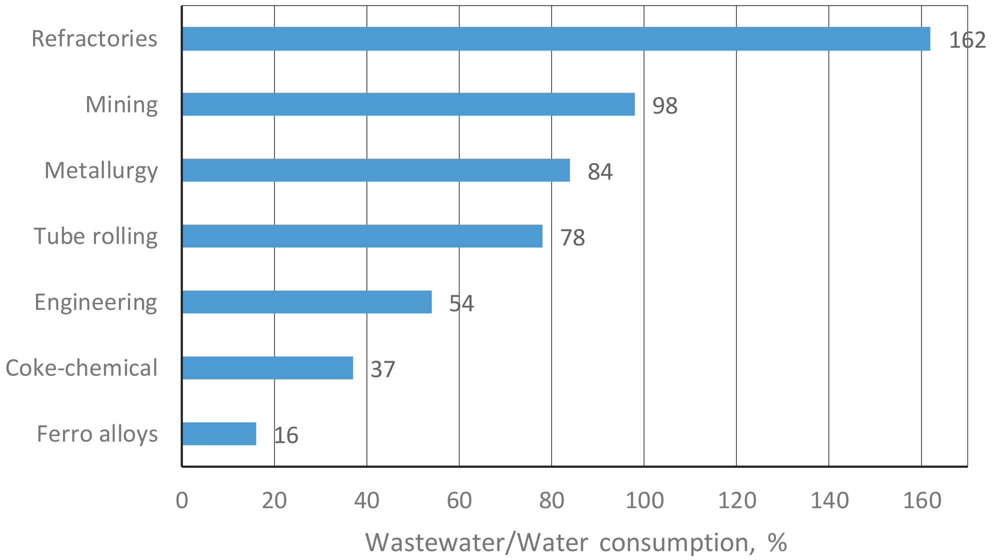

Fig. 3. The annual ratio of wastewater amount and water consumption in heavy industry enterprises in Ukraine

Source: based on [20]

The aim of this paper is to assess the impact of wastewater discharged from the Azovstal Iron & Steel Works (AI&SW) on the coastal waters of the Sea of Azov according to the assessment methodologies established by the Ukrainian legislation, which is currently in force.

2. Characteristics of the Azovstal Iron & Steel Works

Metallurgical industry is a strategic branch of heavy industry in Ukraine. Azovstal Iron & Steel Works (AI&SW) is the largest metallurgical enterprise in the south-east of Ukraine and located on the shores of the Sea of Azov in Mariupol. It includes four primary production complexes: Coke-Oven and By-Products Plant, Ironmaking, Steelmaking and Rolling Complexes. The area occupied by the plant is 1,111.74 hectares, which is more than 7% of Mariupol's total area (Fig. 4)

AI&SW is a part of Metinvest Holding owned by the System Capital Management group, which takes the 45th place in the world ranking of the largest steel producers according to the International Metallurgical Association World-steel data [22]. The crude steel production by Metinvest Holding decreased in the period 2011–2021 repeating the general trend of crude steel production in Ukraine (Fig. 5).

Fig. 4. Location of Azovstal Iron & Steel Works
Source: based on [36, 37]

The water intake for industrial and sanitary-hygienic purposes of AI&SW takes place from nearby water bodies – the Sea of Azov and the Kalmius River (Fig. 4) and amounted to about 700 million m^3/year. Sea water is mostly consumed for heat-exchanging processes. Wastewater generated in technological and heat-exchanging processes are discharged through three outlets to the coastal zone of the Sea of Azov (Fig. 6). Heat-exchanging wastewater is discharged into the Sea of Azov through discharge 1 and 2, while industrial wastewater (about 40% of the total amount of wastewater discharged) – is via discharge 3.

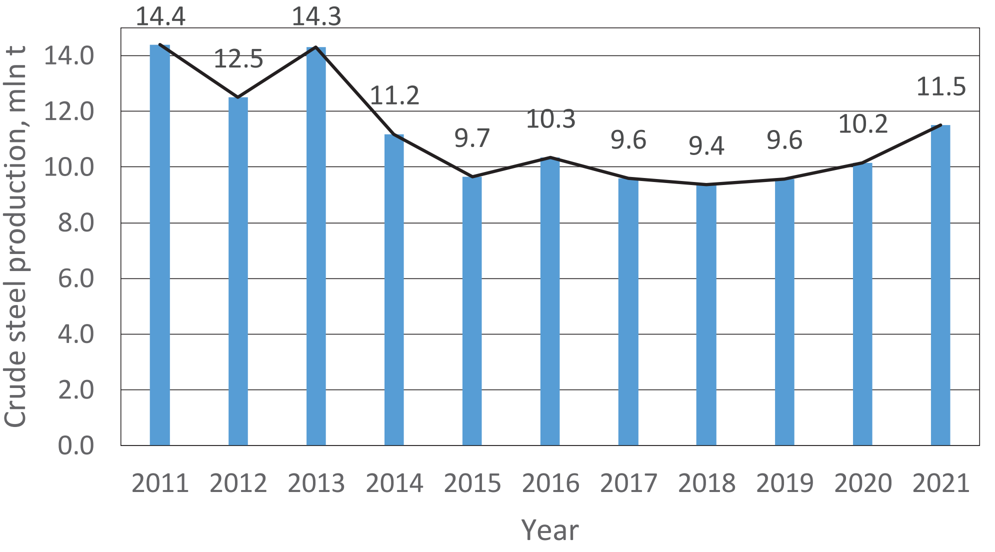

Fig. 5. Metinvest Holding crude steel production in the period from 2011 to 2021

Source: based on [22–32]

Fig. 6. Metallurgical wastewater discharge points (1, 2, 3) into the Sea of Azov

Source: based on [38]

Sea water quality monitoring in the area of wastewater discharge is carried out by the AI&SW enterprise at appropriate control points (CP1, CP2, CP3) at a distance of 250 m from the point of wastewater introduction (Figs. 6, 7).

Fig. 7. Metallurgical wastewater discharge points (1, 2, 3)
and the corresponding control points (CP1, CP2, CP3)

Source: based on [38]

The characteristics of wastewater discharged via discharge points 1–3 (Fig. 7) to the sea recipient is presented in Table 2.

Table 2. Characteristics of wastewater discharged into the Sea of Azov

No.	Wastewater category	Wastewater source	Wastewater flow intensity [m^3/hour]
1	heat-exchanging	Water after heat-exchanging heat-and-power engineering equipment of steam electric blower station and heat-electric generating station	22,000
2	heat-exchanging	Water after heat-exchanging equipment of the oxygen department	1,100
3	industrial	Industrial wastewater from the blast furnace, gas, blooming mill, rail and structural steel mill and large sections department, drain wastewater through a sludge collector	16,000

The large loads of pollutants discharged from the territory of AI&SW led to the disturbance of the ecological situation of the coastal zone of the Sea of Azov receiving industrial wastewaters [18, 39].

3. Characteristics of the Wastewater Recipient

The Sea of Azov is one of the smallest and shallowest seas on the planet and is characterized by a low salt content of about 12–14‰. It is situated in the eastern part of Europe (Fig. 8). The geographical border of the Sea of Azov lies between the points: 47°17′N and 39°49′E in the northeastern part of the Taganrog Bay, 39°18′E in the west (the Arabat Spit) and in the south of the Strait of Kerch (45°17′N) between the Cape Takil and Cape Panagia. According to various estimations, the surface area of the Sea without the Sivash lagoon system and eastern coast estuaries is 37,600–39,100 km^2. The average water volume is about 290–320 km^3. The Sea is 380 km long and 200 km wide; the average depth is 7 m with a maximum value of 14 m. The vast majority of the exchange of waters of the Sea of Azov occurs through the Kerch Strait with the Black Sea. According to long-term average data, 49.2 km^3 of water flows out of the Sea of Azov annually, and 33.8 km^3 of Black Sea water per year enters it. The resulting runoff of water from the Sea of Azov to the Black Sea, on an average long-term value, is 15.5 km^3/year [40–44].

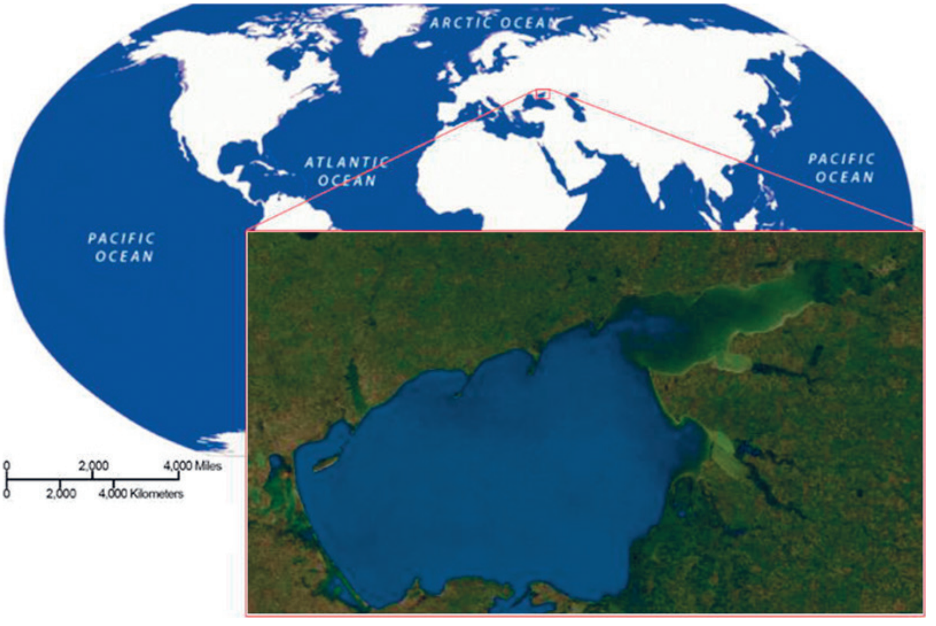

Fig. 8. Geographic position of the Sea of Azov

Source: based on [45]

In spite of its small size, the Sea of Azov plays an important role in the economic development of the adjacent territories. The Sea of Azov and its coastal areas are used for industrial, transport, commercial, agricultural, tourist and recreational purposes and other activities [41]. Therefore, the sea is under the pressure of significant anthropogenic loads, seen primarily in salinity changes, the disturbance of the ecological situation and the deterioration of water quality. One of the most dangerous sources of pollution are metallurgical industry enterprises.

The unsatisfactory ecological situation of the Sea of Azov, caused by the economic activity of neighboring countries in the last decade, is one of its most significant problems. Before the collapse of the Soviet Union the water protection measures were far from perfect, but were fairly correct and generally implemented [46]. Yet environmental protection activities in the last 10 years have largely been abandoned. As a result, pollution loads have increased in connection with the discharge of domestic and industrial wastewaters, shipping and agricultural activities. These are the reasons for the current environmental problems of the Sea of Azov. The most important anthropogenic factors that have a significant negative impact on the Sea of Azov ecosystem are the following: industrial and municipal wastes; oil products; coastal and dam construction; agriculture; bottom trawling; poaching [41, 47, 48].

One of the most important barriers in the protection of the Azov Sea is an insufficiently developed monitoring system and the lack of regular sea state assessment and water quality, both at the state and local levels. However, the assessment of industrial-influenced surface waters ecological state is relevant and necessary, since it allows not only to determine the degree of negative impact, but also to elaborate the appropriate water management and protection solutions to reduce the negative anthropogenic influence.

4. Assessment Methodology

The assessment of any type of surface water state is carried out in accordance with specific methodologies and based on legally approved quality standards [49].

Water policy in Ukraine is regulated by the following legislation documents [50]: Water Law of Ukraine [51]; Law of Ukraine on Environmental Protection [52]; Conditions for industrial wastewater discharge to the municipal sewage system [53] and others. The legislation applies to all types of water bodies existing on the territory of Ukraine: surface and ground waters, and internal sea waters and is the basis for the development of management strategy [54].

The legislation of Ukraine sets standards for the quality of surface waters in the form of maximum permissible concentrations of pollutants (MPC) in fresh and marine waters depending on water use category.

The main principle of water quality assessing, which has been used for a long time in the water protection practice of Ukraine, consists in comparing the values of the fixed set of parameters characterizing the chemical composition, physical properties, and bacteriological characteristics of water in monitoring points with the appropriate standard values of the corresponding indicators. This methodology is described in detail in [54]. However, for all its apparent simplicity, this method cannot become a reliable tool for water state assessment and its quality classification due to the following factors: imperfection of laboratory research methods and the lack of consideration of specific hydrological, morphological, hydrobiological and hydro chemical properties of individual types of water bodies [18, 55].

Thus, the MPC values were developed for seawater do not always provide a reliable basis for assessing the state and quality of the water of the Sea of Azov. A much more reliable assessment method of sea water state and quality is based on integrated numerical indicators, considering the impact of the most dangerous substances. Such indicators include: Water Quality Index (WQI), Water Pollution Index (WPI) and Ecological State Index (ESI) [2, 55–65].

Thus, the assessment of the state and classification of the water quality of the Azov Sea in the industrial-influenced water area was based on the current assessment methodologies and indexes actually in force in Ukraine [66].

The assessment was based on the averaged data of the coastal water monitoring for the period 2016–2021 which was conducted in the framework of cooperation between AI&SW, Pryazovskiy State Technical University (Ukraine) and AGH University of Science and Technology (Poland).

The assessment of the Sea of Azov state around AI&SW impact was carried out based on the integral numerical indexes: Water Quality Index (WQI), Water Pollution Index (WPI), and Ecological State Index (ESI), considering the "limiting criterion principle" [55–57, 60–64, 67]. This principle established by legislation acts of Ukraine [60] assumes the division of all water pollutants into four classes according to the level of their hazard impact on water quality:

I class – extremely dangerous,
II class – highly dangerous,
III class – dangerous,
IV class – moderately dangerous.

Such classification of substances is considered for the following purposes:

- to establish the priority of water quality indicators,
- for planning key water protection investments,
- to develop the clean industrial technologies.

In order to consider the synergistic effect of several highly dangerous substances (of I and II hazard class) discharged into surface waters, their total content must comply with the following requirement (1) [60]:

$$\frac{C_1}{\mathrm{MPC}_1} + \frac{C_2}{\mathrm{MPC}_2} + \ldots + \frac{C_n}{\mathrm{MPC}_n} \leq 1 \tag{1}$$

where C_1, C_2, ..., C_n – concentrations of substances of I and II hazard class.

4.1. Assessment based on WQI

For water quality evaluation in accordance with the regulations of GOST 27065-86 *Water quality. Terms and Definitions* [63] the Water Quality Index (WQI) is used, which allows an integral assessment of sanitary water quality on the basis of key indicators combination and water use category [68, 69]. The WQI is calculated using the Equation (2) [67]:

$$WQI = \sum_{i=1}^{p} \gamma_i \cdot \omega_i \text{ provided } \sum \gamma_i = 1 \qquad (2)$$

where:

γ_i – the weight of the indicator included in WQI,
ω_i – points (from 1 to 5), assigned to each indicator included in the general sanitary WQI,
p – indicators included in WQI,
γ_i, ω_i – values established in accordance with Table 3 [67].

Table 3. Water Quality Index (WQI)

Indicator	Weight of indicator (γ)	Points (ω)				
		5	4	3	2	1
Coli index	0.18	0–100	101–1000	10^3–10^5	10^5–10^7	>10^7
Smell, points	0.13	0	1–2	3	4	5
BOD_5 [mg O_2/L]	0.12	<1.0	1.0–2.0	2.1–4.0	4.1–10.0	>10.0
pH	0.10	6.5 < pH ≤ 8.0	6.0 < pH ≤ 6.5 8.0 < pH ≤ 8.5	5.0 < pH ≤ 6.0 8.5 < pH ≤ 9.5	4.0 < pH ≤ 5.0 9.5 < pH ≤ 10.0	pH < 4.0 pH > 10.0
Dissolved oxygen [mg O_2/L]	0.09	>8	8–6	6–4	4–2	<2
Chromaticity [°]	0.09	<20	21–30	31–40	41–50	>50
Suspended solids [mg/L]	0.08	<10	10–20	21–50	51–100	>100
Total mineralization [mg/L]	0.08	<500	500–1000	1,001–1,500	1,501–2,000	>2,000
Chlorides [mg/L]	0.07	<200	200–350	351–500	501–700	>700
Sulfates [mg/L]	0.06	<250	250–500	501–700	701–1,000	>1,000

Source: [67]

Classification of water quality is determined according to WQI values presented in Table 4.

Table 4. Water quality classification on the base of WQI value

WQI values	Water quality class	Water quality
5.0	1	very pure
4.1–4.9	2	pure
2.6–4.0	3	moderately polluted
1.6–2.5	4	polluted
≤1.5	5	dirty

Source: [67]

4.2. Assessment Based on WPI

The Water Pollution Index (WPI) was developed by the Hydrometeorology State Committee [70] and belongs to the category of aggregated indicators for comprehensive assessment of water pollution level. This index is a typical additional assessment method and represents the averaged level of MPC exceedance for strictly limited set of parameters for the corresponding type of water bodies. Calculation of WPI for sea waters is carried out according to the Equation (3) [62]:

$$\mathrm{WPI} = \left(\sum_{i=1}^{n} \frac{C_i}{\mathrm{MPC}_i} \right) \Big/ 4 \tag{3}$$

where:

n – strictly limited number of parameters of significant environmental impact, regardless of their compliance with the MPC,
C_i – pollutant concentration in water,
MPC_i – maximum permissible concentration of pollutant.

Water quality classification according to WPI value is presented in Table 5.

Table 5. Sea water quality class according to WPI value

WPI value	Water quality class	Water quality
<0.25	1	very pure
0.25–0.75	2	pure
0.75–1.25	3	moderately polluted
1.25–1.75	4	polluted
1.75–3.00	5	dirty
3.00–5.00	6	very dirty
>5.00	7	extremely dirty

Source: [64]

4.3. Assessment Based on ESI

The Ecological State Index (ESI) refers to the indicators that allow a large number of factors affecting the ecological status of water bodies to be taken into account and is calculated by the Equation (4) [67]:

$$ESI = \frac{1}{n_b} \cdot \sum_{i=1}^{n_b} b_i \tag{4}$$

where:

n_b – number of parameters used to calculate the index,
b_i – points (from 1 to 4), assigned to each indicator depending on the range of its values in accordance with Table 6.

Table 6. Weight of individual indicators

Indicator	Point (b)			
	1	2	3	4
MPC [mg/L]	<0.01	0.01–0.10	0.11–1.00	>1.00
Class of danger	I	II	III	IV
WQI	<1.6	1.6–2.5	2.6–4.0	>4.0
WPI	>4.0	2.1–4.0	1.0–2.0	<1.0

Source: [67]

The classification of the ecological state of water bodies on the basis of the ESI value is presented in Table 7 [67].

Table 7. Classification of water bodies depending on ESI values

ESI value	Water quality class	Ecological state
≤1.69	I	ecological disaster
1.70–2.39	II	ecological crisis
2.40–2.99	III	ecological stress
≥3.00	IV	relatively good condition

Source: [67]

5. Results

The assessment was conducted in order to identify the scale of the negative impact of wastewater discharge of metallurgical enterprise AI&SW on the basis of water monitoring results at chosen control points CP1, CP2 and CP3 Fig. 7).

In accordance with [60], the quality of the Sea of Azov waters must comply with MPC standards. Table 8 presents the established permissible concentrations of the main pollutants, concentrations of the same pollutants in control points and the degree of standards exceeding.

Table 8. The degree of MPC exceedance at monitoring points

Pollutants	MPC [mg/L] [55, 60]	Concentration [mg/L]			CP/MPC		
		CP1	CP2	CP3	CP1/MPC	CP2/MPC	CP3/MPC
Oil products	0.05	0.180	0.143	0.228	3.6	2.9	4.6
Iron total	0.05	0.187	0.192	0.258	3.7	3.8	5.2
Ammonia	0.50	0.721	0.875	0.933	1.4	1.8	1.9
Nitrites	0.08	0.164	0.075	0.208	2.1	0.9	2.6

The results of the assessment presented in Table 8 show a significant exceedance of pollutants content in receiving waters influenced by the industrial wastewaters from AI&SW enterprise.

The greatest exceedance of MPC standards was observed in CP3 which is located in the zone of industrial wastewater discharge. At the heat-exchanging water discharge points (CP1 and CP2), the negative impact was slightly smaller.

Then, the total highly dangerous pollutants content compliance (nitrites, cobalt and lead – II hazard class) with the principle of limiting criterion was assessed. The pollutants of I hazard class were not detected. The results of the assessment are presented in Table 9.

Table 9. The results of the assessment according to according to "limiting criterion" principle for highly dangerous substances

Pollutants	MPC [mg/L]	CP1	CP1/MPC	CP2	CP2/MPC	CP3	CP3/MPC
Nitrites [mg/L]	0.08	0.164	2.05	0.075	0.94	0.208	2.60
Cobalt [mg/L]	0.13	0.0028	0.02	0.0028	0.02	0.0028	0.02
Lead [mg/L]	0.03	not found		not found		0.015	0.43
Σ (C_{CP}/MPC) < 1		2.05		0.96		3.05	

The condition for the “limiting criterion” principle was only fulfilled for CP2. The maximum index value was set for CP3 (industrial wastewater), which confirmed the highest negative impact of technological wastewater discharge.

Thus, it has been established that the water quality of the Sea of Azov in the area of AI&SW wastewater discharges, assessed with consideration of the “limiting criterion” principle, does not meet the legal demands which proves about the negative impact of the AI&SW enterprise on sea water in the zone of wastewater discharge.

6. Classification of Sea Water State

A comprehensive assessment of sea water state in the zone of wastewater discharge from AI&SW was based on the numerical integrated indicators.

The sanitary condition of sea waters was assessed on the basis of the calculated values of WQI in the points CP1, CP2 and CP3 taking into account the concentrations of suspended solids, total mineralization, chlorides, sulfites, BOD_5 and pH values. The results are presented in Table 10.

Table 10. Water quality index WQI in control points

Indicator	CP1	CP2	CP3	Weight (γ)	Points (ω)	γ · ω		
						PPK_1	PPK_2	PPK_3
BOD_5 [mg O_2/L]	2.22	2.18	2.33	0.12	3	0.36	0.36	0.36
pH	7.95	7.92	7.88	0.10	5	0.50	0.50	0.50
Suspended solids [mg/L]	24.5	23.0	28.1	0.08	3	0.24	0.24	0.24
Total mineralization [mg/L]	7,989	8,024	8,186	0.08	1	0.08	0.08	0.08
Chlorides [mg/L]	4,798	4,636	4,588	0.07	1	0.07	0.07	0.07
Sulfites [mg/L]	956.5	964.9	963.7	0.06	2	0.12	0.12	0.12
Water quality index WQI						1.37	1.37	1.37

In all control points, WQI values were 1.37. According to Tables 3 and 4, such WQI value corresponds to the 5^{th} class of water quality, which means that water is dirty and its sanitary condition means that it is not suitable for communal and recreational purposes.

For the assessment of the pollution degree of the industrially influenced area of the Sea of Azov, the water pollution index (WPI) was used, which is calculated using the Equation (2). The assessment of water quality in the zone of AI&SW impact (control points CP1, CP2 and CP3) was carried out with WPI for sea waters which is based on four key indicators (BOD_5, total iron, nitrites, and oil products) according to Equation (5) [62]:

$$WPI = \left(\frac{C_{BOD_5}}{MPC_{BOD_5}} + \frac{C_{Fe}}{MPC_{Fe}} + \frac{C_{NO_2}}{MPC_{NO_2}} + \frac{C_{oil\ prod}}{MPC_{oil\ prod}} \right) \Big/ 4 \quad (5)$$

where:

C_n – pollutant concentration in sea waters,

MPC_n – maximum permissible concentration of pollutant.

Calculated WPI values and the degree of MPC exceedance are presented in Table 11.

Table 11. WPI values in the area of wastewater discharges

Concentration [mg/L]	MPC	CP1	CP1/MPC	CP2	CP2/MPC	CP3	CP3/MPC
BOD_5	3.00	2.21	0.74	2.19	0.73	2.37	0.79
Iron total	0.05	0.187	3.74	0.192	3.84	0.258	5.16
Nitrites	0.08	0.164	2.05	0.075	0.94	0.208	2.60
Oil products	0.05	0.180	3.60	0.143	2.86	0.228	4.56
WPI*		2.53		2.09		3.28	

*Values of WPI for sea waters calculated according to Equations (3) and (5).

The results of water quality class classification in the points of wastewater discharges according to Table 5 compared to the background conditions in the open sea are presented in Table 12.

Table 12. The results of water quality class assessment in the area of wastewater discharges

Parameter	Discharge no.			Background value in Sea of Azov open waters [71]
	CP1	CP2	CP3	
WPI value	2.53	2.09	3.28	0.60
Quality class	dirty	dirty	very dirty	pure

It implies that the enterprise has a negative impact on coastal water quality, which is characterized by a significantly higher level of pollution than open sea waters. The greatest negative impact is observed in the zone of the technological wastewater discharge.

In order to assess the general ecological state of the Sea of Azov in the zone of industrial wastewater discharge, the ecological state index ESI was calculated. The results of ESI assessment are presented in Table 13.

Table 13. Integral index of ecological state for CP1–CP3

Constituent parameters	Control points		
	CP1	CP2	CP3
MPC [mg/L]	4	4	4
Class of danger in water	3	3	3
WQI, points	1	1	1
WPI, points	2	2	2
ESI	2.5	2.5	2.5

ESI values calculated for all control points are 2.5, which corresponds to the III ecological class and corresponds to ecological stress.

7. Conclusions and Recommendations

The metallurgical industry is a branch of the economy with a strong negative environmental impact at both the local and the regional scales. Metallurgical plants generate large amounts of dangerous wastewaters and wastes which is discharged into water recipients.

The results of the assessment based on WQI, WPI and ESI indexes and the "limiting criterion principle" as well as on the sea water quality standards in force in Ukraine, allowed us to conclude that the sea water area under wastewater influence is characterized by poor sanitary conditions, a high level of pollution and is under ecological stress. It is not suitable for communal and recreational purposes. The obtained assessment results suggest that the sea waters in the coastal zone are strongly influenced by the AI&SW metallurgical enterprise. It is especially visible against the background of the open sea area quality, which is characterized as pure water.

The most unfavorable effect is observed at the control point CP3, where technological wastewaters with high content of hazardous substances is discharged. Here the concentrations of pollutants significantly exceed the permissible levels and the quality of water significantly worth than in the points CP1 and CP2 to which the heat-exchanging wastewater is discharged.

The most dangerous substances in the composition of the wastewater discharged into the Sea of Azov are iron, nitrites and oil products, which leads to exceeding the normative values of these substances in the marine environment and the resulting negative consequences. Therefore, measures aimed at reducing the negative impact of wastewaters from the AI&SW on the recipient should focus primarily on the efficient removal of these substances prior to discharge.

However, the protection of the marine environment in the Azov Sea in the AI&SW's impact zone should be implemented based on a system approach with the priority measures according to the principles of the following scheme (Fig. 9).

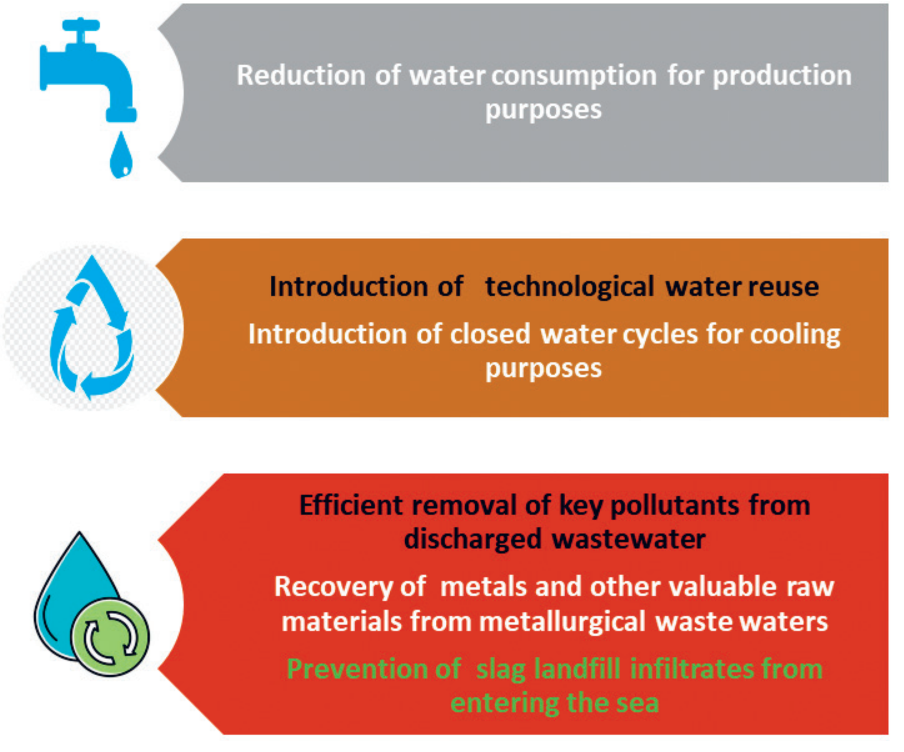

Fig. 9. The proposition of water protection agenda for AI&SW metallurgical enterprise

The assessment of ecological state of industrial-influenced surface waters is relevant and necessary, since it is the base for identification of their negative impact and elaboration of the appropriate water management and protection solutions in order to reduce negative anthropogenic influence.

The solution to this problem is possible by reducing water consumption, introducing clean technologies and closed water cycles. These undertakings should be accompanied by regular monitoring of wastewater quality and the assessment of its impact on the receiving waters.

Author Contribution

Elena Neverova-Dziopak and Olena Dan: conceptualization, methodology, validation, formal analysis, investigation, resources, data curation, writing – original draft preparation, writing – review and editing, visualization, supervision, project administration, funding acquisition.

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