WATER QUALITY PARAMETERS OF THE BLACK SEA COAST IN NAVODARI – MAMAIA – CONSTANŢA AREA

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Abstract
Our study proposes a physical-chemical parameters comparison of the water from the Black Sea Coast in Navodari – Mamaia – Constanta area, made in purpose of evaluating the human activity influence upon these coastal waters involved in touristic potential. The study was made in the period 2009-2011 in the aim to determine the water quality dynamics in time and pollution level. Specific physical-chemical parameters were determined according the Romanian standard for surface waters. Instrumental, volumetric and gravimetric methods were used. Analytical characterization was supplemented with microbiological studies which shown a different bacteriological charge with respect to seasons and coastal area. The obtained results were compared with existent published data and they contribute to the completion of database information regarding the ecosystem state of the Black Sea Coast.

Keywords: water quality, physical-chemical composition, pollution indicators, Black Sea Coast.

1. INTRODUCTION

It is known from the literature the influence of human activities on the coastal waters involved in touring potential, regarding critical soil pollution on large land areas due to uncontrolled dumped waste as a result of boom urbanization and lack of an overall development plan. Taking into consideration the uncontrolled dumped waste, the heavy rains could transport harmful substances to the surface waters and then in the sea (Abaza, 2010; Dumitrescu&Telembici, 1995).

The excessive pollution of Black Sea waters, especially in the NW part of the basin (including the Romanian coastal zone) resulted in a strong eutrophication of the sea due to the nutrients coming from different activities. Only the Danube River yearly conveyed around 60,000 tons of phosphorus and 300,000 tons of inorganic nitrogen. Also, as a result of chemical fertilization in agriculture and using at a large scale the detergents with phosphates, in the last 25 years a dramatic increase of nutrients in the Black Sea has been registered. Another cause of eutrophication due to the presence of nutrients and organic matters refers to the untreated or insufficient treated waste waters from zootechnical facilities or inefficient waste water treatment plants. If we added the fact that 70-80 % from the length of the littoral is affected by erosion – in the last 30 years, the shoreline corresponding to the Biosphere Danube Delta reservation is withdrew in some parts with around few hundred meters and losing yearly around 80 hectares from the beach – we could have a complete image of the existing situation. The pollution of the shoreline (dry land part) and the development discrepancy affected the touristic resources, areas of scientific importance (natural reservations and protected areas) and archaeological sites (Postolache, 1973; Rădulescu et al., 1980; Iordache et al., 1997).

The pollution of shoreline waters by industrial and harbor activities, generated the increasing of heavy metals content and organic-chlorinated substances, due to lack of the facilities in order to receive the waste waters from the ballast tank cleaning, accidentally pollution during the loading and unloading ships and which add the fact that the Danube River annually brings in the Black Sea an equivalent of 45,000 tons of oil products, all these factors contributed to a grim picture regarding the actual state of the Black Sea waters. The literature data analysis (Popa & Cociasu, 1994; Popa, 1994) underlined the Danube river importance as source of continue carried organic and inorganic matter (Table 1).

Table 1. The average concentration of annualy nutrient carried in the Danube river waters

Average	PO_4	NO_3	NO_2	NH_4
Concentration (µM)	4,894	285,166	1,65	6,95
Quantity (thousand tons)	24,28	704,74	3,956	15,206

The accumulations of these components in the south of littoral are strictly connected with the presence or absence of the consumers because of the decreasing of the mineral components from Sulina to Mangalia, the determinant role of the Danube river as carrier and the stabilization tendencies of the sea waters by dilution and living component have been observed (Rojanschi et al., 1997; Valiela, 1995).

This study presents a comparison between the physical-chemical and microbiological parameters of the Black Sea waters in area Navodari-Mamaia-Constanta, during last three years (period 2009-2011) with purpose to mark out the water composition dynamics and to append our results to existing literature data.

2. METHODS

Sea water samples were collected from four different stations, important touristic area, distinctly influenced by human activities and environmental factors: Navodari Children Camp, Mamaia resort, Pescarie Constanta. Because of the fact that the waters are less disturbed by the human crowding summer, was chosen the September month as observation time in the period of years 2009 — 2011, after the summer season's impact of the environmental. The sampling was done weekly in the entire studied area. Were analyzed the main physical-chemical indicators which characterized eutrofication level.

The physical and chemical analyzes were carried out according Romanian standard methods for the category IInd bathing surface waters, as following: *p*H, electrical conductivity, temperature (instrumental method), total amount of suspension matters and fixed residue (gravimetric methods), organic substances (titrimetric methods), chlorides, sulfates, calcium (gravimetric and titrimetric methods), nitrates, nitrites, phosphates, ammonia, total iron (UV-VIS molecular absorption spectrometry) (NTPA001/2002), Romanian HG 546/2008; Pătroescu&Gănescu, 1980).

Apparatus:
- Multichannel Analyzer WTW;
- Molecular absorption spectrophotometer UV-VIS Cecil CE3200 Super Aurius

The sea water and sand for microbiological samples were collected from the same stations and analyzed according on Romanian Standards methods (NTPA001/2002, STAS 4706/88). Intestinal enterococci and *Escherichia coli* were determined using standard methods on solid and liquid medium and for *Giardia intestinalis* cysts, microscopic determination after concentration and coloration with Lugol solution. Were not pursued only the isolation of the „classical" indicators of surface waters pollution foreseen in the standards (NTG, total coliforms, faecal coliforms, enterococci), but a particular importance having the determination of pathogen species or conditioned pathogens as *Pseudomonas aeruginosa*, which has carried out by serotyping with Sanofi Pasteur agglutinant serums, the determination of pathogen groups from the genus of *Salmonella*, determination of species with API kits (for enterococci and *Salmonella* sp.), Sanofi Pasteur kits for *Candida* strains determination and ELISA kits for *Giardia intestinalis* cysts detecting in environment samples (Merck Microbiology Manual, 1996).

3. RESULTS AND DISCUSSION

Compared with literature data, our results show that the physical-chemical parameters correspond to Romanian Standard for the analyzed indicators. In the Table 2 is presented the values average registered for the principal indicators of the Black Sea, in the period 2009-2011.

Table 2. Black Sea water indicators values average registered for in the period 2009-2011

Indicators	Analysis method	Admissible values *)	Black Sea water samples – experimental data		
			2009	2010	2011
Color	SR ISO 7980-97	Normal	normal	normal	normal
Temperature	SR ISO 10523-97 STAS 7722-84	35	22	24	21
*p*H		6-8.5	8.2	8.1	8.4
Electrical conductivity, μS/cm, max		2500	20500	21200	21500
Salinity (‰)		-	16,77	17,80	18,40

Ammonia, mg/dm^3	STAS 8683-70	2,0	0,540	0,343	0,198
Nitrates, mg/dm^3	STAS 8900/1-71, SR ISO 7890/1-98	25,0 (37,0)	0,360	0,381	0,370
Nitrites, mg/dm^3	STAS 8900/2-71 SR ISO 6777-96	1,0 (2,0)	0,064	0,074	0,066
Ca^{2+}, mg/dm^3	STAS 3662-90 SR ISO 7980-97	300	152.3	150.9	151.9
Chlorides, mg/dm^3	STAS 8663-70	Not defined	8564.8	8420.8	8572.5
Sulphates , mg/dm^3	STAS 8601-70	600	170.9	171.5	182.3
Phosphates, mg/dm^3	STAS 10064-75 3/86	Not defined	0,138	0,126	0,120
Total ionic iron, mg/dm^3	SR ISO 6332-96	5,0	0.1	0.1	0.1
Dissolved O$_2$, mg/dm^3	STAS 6838-88	6,0	6.2	7.21	6.44
Fixed residue, mg/dm^3	STAS 9178-84	2000	16100	16093	16155
Organic matter (oxidability), mg/dm^3	STAS 3002-85	15	4,75	8.71	8,83

*) – Romanian Standard - STAS 4706-88 - Surface Water IInd category

From the obtained results it can be noticed the variation of concentration of some specific physical and chemical parameters, correlated with initial sources activity. In the observation period of three years (2009-2011), is highlighted the year 2009 which includes a maximum concentration of phosphates and a minimum concentration of nitrites and nitrates and also thermal homogeneity (Table 3).

Table 3. The main physical and chemical characteristics of Black Sea waters in Mamaia area
September 2009

Parameter	Năvodari Camp	Alcor Hotel	Casino Mamaia	Pescarie Constanta
Temperature (°C)	22	22	22	22
Salinity (‰)	16,59	16,74	16,49	16,88
Organic matter (mg/ dm^3)	3,09	3,40	3,30	8,40
Nitrates (mg/ dm^3)	0,400	0,362	0,293	0,384
Nitrites (mg/ dm^3)	0,060	0,078	0,045	0,066
Ammonia (mg/ dm^3)	0,6550	0,9870	0,1090	0,4110
Phosphates (mg/ dm^3)	0,4550	0,8573	0,7820	0,8610

The salinity values have not major oscillations in time, but increased values in some areas with maximum values in the Pescarie Constanta area and minimum values in the Casino Mamaia area. The organic matter has minor oscillations in time but with maximum values in the Pescarie Constanta area. Regarding the nutrients (phosphates, nitrates, nitrites, ammonia salts - Table 3) it can be noticed a certain distribution diversity which indicates the Casino Mamaia area with maximum values for phosphates and nitrites and Năvodari Camp area with maximum values for nitrates. The highest concentration of ammonia salts was recorded in the Alcor Hotel area. Obviously there is a short observation period but sufficient in order to highlight the dynamics of the areas, especially in the Năvodari Camp and the Casino Mamaia.

As result of the analysis from the period 2009-2011 the variation of concentration of some categories it can be observed, which is certainly correlated with the activity of initial sources. These annually variations showed that the measures which can be taken refer to the generation sources because in the Black Sea waters we could only notice the presence of these substances and their effects.

The dissolved organic matter is related to the food chain and then the variation of this matter is determinant in biological evolution of marine ecosystem. For the same coastal Mamaia area and approximately in the same observation period it can notice in the beginning of autumn, the nitrites accumulation and also of the phosphates.

The chemical data have been correlated with microbiological data. Beginning with the year 2010 has been noticed that the number of samples with bacterial charges (fecal coliforms, enterococci), was increased than in the years 2009 and 2011 (Table 4).

In the period 2009-2011 were analyzed a number of approx. 150 sea water samples/year. The results show that almost 40-70 samples, especially in Mamaia area and Pescarie area in Constanta, were inappropriate. Here were identified *Giardia intestinalis* cysts in eight samples and was isolated *Candida albicans* in four samples.

Table 4. Microbiological indicators registered for the Black Sea water, during 2009-2011 period

Pollution indicators No./ 100 cm^3	Analysis method	2009	2010	2011
Intestinal enterococci	ISO 7899-1, ISO 7899-2	1130	1420	1200
Escherichia coli	ISO 9308-3, ISO 9308-1	116	128	115

The situation of the samples analyzed in the period of 2009 – 2011 is presented in the Table 6.

Table 5. The comparative microbiological results of sea water samples

Year	No. of inappropriate samples according HG 546/2008	Inappropriate samples %
2009	38	23,89
2010	55	29,89
2011	77	47,80

The situation of the sand samples analyzed and the number of isolation *Salmonella* sp. is presented in the Table 6.

Table 6. The situation of *Salmonella* sp. samples presence

Year	No. of samples were identified *Salmonella* sp.
2009	60
2010	50
2011	32

In the same period the analysis of the sand beach showed that the inappropriate percent of sands higher than the inappropriate percent of sea waters and explained by the beach sanitization deficiency. Also, in some littoral areas are shown the increasing of inappropriate water samples percent.

In the Table 7 is presented the percent of *Enterococcus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Candida sp.* and *Giardia intestinalis* cysts isolated from beach sand samples in the period of 2009 – 2011, in the month of September.

Table 7. The dynamics in time of *Enterococci, Escherichia coli, Pseudomonas aeruginoasa, Candida ap.* and *Giardia intestinalis* strains in sand samples

Microbial strain	% registered		
	2009	2010	2011
Total samples	75	35	83
Enterococci	46,66	46,71	45,40
Escherichia coli	12	14,28	8,43
Pseudomonas aeruginosa	1,33	2,85	2,40
Candida sp.	5,13	2,85	4,81
Giardia intestinalis	4	0,00	0,00

4. CONCLUSIONS

1. In the observation period the results could be noticed as a reference panel in the future regarding the increased human pressing;

2. The correlation between physical-chemical and microbiological results suggests the necessity of a complex monitoring able to offer at any time the information refers to water quality, considering of touristic importance the Romanian Black Sea Coast;
3. The comparable level of the results with the literature data and the highlighting of the area dynamics, qualified our results as potential useful information;
4. Our observations in the period of three years, area analyzed and determinations type have indicated the framing values of the examined parameters (salinity, organic matter, nitrites, nitrates, ammonia, phosphates) with some exceeding for fixed residue and suspended solids because of the anthropic influence in the summer time;
5. The association of literature data with time observing data (chemical, microbiological) of the investigated area (Navodari-Mamaia-Pescarie Constanta), could be taken into consideration regarding the ecological status and could contribute to the completion of database informations regarding the ecosystem state of the Black Sea Coast.

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