# **Sea Bottom Sediments Pollution of the Crimean Coast (The Black and Azov Seas)**



**E. A. Tikhonova, E. A. Kotelyanets, and O. V. Soloveva**

**Abstract** The aim of this research was to determine the content of trace elements and heavy metals (HM), extractable organic matter (EOM), total petroleum hydrocarbon content (TPC) in the sea bottom sediments of the Azov and Black Seas, to evaluate the ecological wellbeing of the region. The EOM amount was determined by gravimetric method, the TPC was determined by the method of infrared spectrometry. The metals and metals oxides were determined using XRF spectrometer «Max Spectroscan-G». The bottom sediments near the coast of Crimea (in 2016) were typical of the marine soils in the area. In the Black Sea, there was a trend to a progressive increase in the EOM content, but the bottom sediments were pure according to content of oil products. The content of HM varied in wide ranges. The vicinity to the pollution source did not always determine the zones of their elevated contents. In the Azov Sea, the resulting concentrations at most stations transcended those in the Black Sea. Values of Zn, V, Cr, Co exceeded their natural content in the shelf sediments throughout the expedition track. Ni content in Azov Sea demonstrated the existence of anthropogenic pollution sources.

**Keywords** Sea bottom sediments · Extractable organic matter · Total petroleum hydrocarbon content · Heavy metals · The Black Sea · The Azov Sea

## **1 Introduction**

Current changes in the state of the Azov-Black Sea ecosystem are not only caused by natural factors, but also increased anthropogenic pressure (Petrenko et al. [2015\)](#page-12-0). The existing problems (Petrenko et al. [2015\)](#page-12-0) include pollution of rivers in the catchment area, intake of insufficiently cleaned industrial and domestic sewage, offshore gas

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<sup>©</sup> The Author(s), under exclusive license to Springer Nature Switzerland AG 2021 T. Chaplina (ed.), *Processes in GeoMedia—Volume II*, Springer Geology, [https://doi.org/10.1007/978-3-030-53521-6\\_23](https://doi.org/10.1007/978-3-030-53521-6_23)

production and use of biological resources. These days, sea transport (especially in the Kerch strait), recreation and hydraulic engineering (in particular, the Crimean bridge) provide additional pressure. Given the fact that the Azov-Black Sea basin is an inland water body with limited assimilation capacity, such level of anthropogenic load can lead to disastrous consequences for its ecosystem.

Sea bottom sediments are one of the most informative objects in the water environmental monitoring, especially near the coast. The pollutants incoming for a long time accumulate in the bottom sediments, and serve as an indicator of the ecological state of coastal ecosystems and a kind of integral indicator of the water body's pollution level. In addition, marine sediments participate in circulation of substances and energy. At the same time, they are the habitats of numerous benthic groups.

We selected coastal areas as the most representative for the environmental quality assessment,since they suffer most from anthropogenic activity, which contributes to formation of the special Black Sea ecosystems (Gurov et al. [2015\)](#page-11-0). The study of physical and chemical properties of bottom sediments in the Black Sea, and observation of the processes in the "water – suspended matter – bottom sediments" system are an important part of the overall monitoring of coastal water areas (Gurov et al. [2015\)](#page-11-0). The Sea of Azov is closed, shallow and suffers from increased anthropogenic load, so monitoring studies are necessary for decision making on maintaining its biological productivity.

Thus, the purpose of this research was to determine the content of trace elements and heavy metals (HM), extractable organic matter (EOM), total petroleum hydrocarbon content (TPC) in the sea bottom sediments of the Azov and Black Seas (including the north-western shelf, the Southern Coast of the Crimea (SCC), the Kerch Strait, the south-west of the Sea of Azov) to assess the ecological wellbeing of the water areas.

## **2 Materials**

The samples were obtained in the 83rd voyage of the R/V "Professor Vodyanitsky" (winter 2016) at the stations (st.) (Fig. [1\)](#page-2-0) located along the Crimea peninsula coast from the depth 24–1040 m in the Black sea and 9–18 m in the Azov sea.

Sea bottom sediments were collected with an automatic box-bottom grab ("Box corer") from an area of  $25 \times 25$  cm. The upper 5 cm layer was used for the analysis. 11 samples were taken in the Black Sea (st. 2–15, st. 20, 21) and 4 in the Sea of Azov (st. 16–19). All the samples were packed in special containers and labeled.



<span id="page-2-0"></span>**Fig. 1** Sampling stations of R/V "Professor Vodyanitsky" (83th voyage)

#### **3 Methods**

The pH and Eh values were measured in the just collected samples of bottom sediments on board using a Neutron-pH pH-meter. Under the laboratory conditions, the sediments were dried to an air-dry state and triturated in mortar. A part of each sample was sieved through sieves with a cell diameter of 0.25 mm to determine the concentrations of TPC and EOM; for HM a 0.071 mm nylon sieve was used. The total amount of EOM in the prepared samples was determined by the gravimetric method, TPC – IF-spectrometry method (SPM-1201) (Oradovskiy [1977\)](#page-12-1). The total content of HM (Cr, Zn, Pb, As, Co, Sr, Ni, V) and metal oxides (MnO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>) was measured by the method of X-ray fluorescence analysis using the spectrometer "Spectroscan Max-G" (Methods… [2002\)](#page-12-2). All the results obtained for the concentrations of organic compounds were recalculated for 100 g of air-dry bottom sediments (air-dryb.s.).

The calibration characteristics for HM were plotted using certified samples of soil composition: typical black humus earth, sod-podzolic sandy-loam soil, red soil, and carbonate grey soil. The control samples (state standard samples of composition SSSC 163.1-98 and the SSSC 163.2-98) (Methods… [2002\)](#page-12-2) were used to check the plot calibration correctness.

Currently, there are no national maximum permitted concentrations for the content of HM in marine sediments. Therefore, the concentrations of trace elements in bottom sediments are usually compared with either their Clarke numbers or background values for the studied marine systems (Methods… [2002;](#page-12-2) Mitropolskiy et al. [1982\)](#page-12-3). Correlation analysis was made in "MS Excel 2003" and "Statistica".

## **4 Results and Discussion**

According to the data obtained, the content of EOM in the bottom sediments of the Black Sea was from 10 to 110 mg/100 g air-dry b. s. The concentration of TPC at most stations ranged from 1.7 to 10 mg/100 g. In the Azov Sea, thevalueswere higher (107 to 187 mg/100 g for EOM). This correspond the sea bottom sediments to III-rdpollution level (Mironov et al. [1986\)](#page-12-4). The TPC concentrations were in the same range as in the Black Sea (6.9–10.2 mg/100 g).

At the st. 7 in the Black Sea the highest values (Table [1\)](#page-3-0) of HM (zinc, cobalt, chromium) content (44% of the samples) in the bottom sediments were noted. The amount of strontium and arsenic being close to the maximum values in the pre-strait zone (st. 15).

Element	Variation limit		Average value	Content in the shelf sediments
	Minimum	Maximum		(Emelyanov et al. 2004)
<b>Black Sea</b>				
Zn, mg/kg	50.1	144.0	81.0	48
Ni, mg/kg	24.7	49.0	40.1	42
Co, mg/kg	35.0	164.7	71.0	14
Cr, mg/kg	84.0	178.8	124.3	$45 - 90$
V, mg/kg	58.1	324.7	162.1	90
As, mg/kg	8.6	130.4	57.4	$5*$
Sr, mg/kg	200.0	3085.0	666.1	$300*$
$TiO2,$ %	0.606	1.62	0.98	$0.6 - 0.8$
$Fe2O3$ , %	3.16	10.35	6.3	5.08
MnO, $%$	0.028	0.06	0.04	0.38
AzovSea				
Zn, mg/kg	84.0	195.2	117.2	48
Ni, mg/kg	45.0	54.4	48.1	42
Co, mg/kg	30.8	300.3	115.5	14
Cr, mg/kg	103.7	259.7	155.2	$45 - 90$
V, mg/kg	98.6	421.3	200.3	90
As, mg/kg	0.5	60.7	42.2	$5*$
Sr, mg/kg	174.6	433.0	276.2	$300*$
TiO <sub>2</sub> , %	0.8	2.2	1.22	$0.6 - 0.8$
$Fe2O3$ , %	5.3	16.1	8.61	5.08
MnO, %	0.05	0.083	0.07	0.38

<span id="page-3-0"></span>**Table 1** Content of heavy metals in the bottom sediments of the Black and Azov Seas (Tikhonova et al. [2016\)](#page-12-5)

\*Concentrations according to B. V. Vinogradov (Dobrovolskiy [2003\)](#page-11-1)

The highest amount of strontium was found at st. 15, which is most likely due to the soil texture (70% of shells), and zinc—at st. 21, near the sewage pipe of Yalta city. Lead was only found near the Karadag mountain range (st. 12). The lowest content of zinc, cobalt, chromium, vanadium and strontium was noted at st. 2 in the Kalamitsky Bay, arsenic—in the reserved water area of Karadag, nickel—in the bottom sediments of st. 15 before the entrance to the Kerch Strait.

The obtained values in the Sea of Azov at most stations exceeded those in the Black Sea, in particular, st. 16 recorded the maximum content of HM. The lowest concentration of HM was noted at st. 17 (50% of indicators), zinc and nickel at st. 19, and arsenic at st. 18.

It is known that the coastal zone is subject to hydrocarbon pollution more than other facies. The constant flux of allogenic material from various sources increases their concentration in bottom sediments. The nature of spatial distribution of pollutants, HM in particular, depends on a complex of natural and man-made factors, with sources of pollution, their power and mode being primary factors.

The sea bottom sediments studied in the framework of the 83rd expedition of the R/V "Professor Vodyanitsky" were typical of the muddy sediments mixed with shell rock and sand, which accumulate to a large extent both natural organic matter and allochthonous compounds. At some stations (st. 9, 14, 16, 18, 20) a whiff of hydrogen sulfide was noted. The bottom sediments at the Black Sea stations were consistently getting finer with depth.

The active reaction of the medium in the the Black Sea bottom sediments was slightly alkaline and the pH ranged from 7.53 to 7.82 (Fig. [2\)](#page-5-0), with the exception of st. 2 near Yevpatoria, where the pH value increased to 8.42, which is most likely due to the type of sedimentation and the close recreation zone.

The redox potential directly depends on the distribution of bottom sediments particle size (Mironov et al. [1992\)](#page-12-6). The reducing conditions of the environment (negative Eh) were found in the bottom sediments at two stations (st. 16—the shallow water station in the Sea of Azov  $(11 \text{ m})$  and st. 20—the deepest station in the Black Sea (1040 m)) with Eh values  $-165$  and  $-174$  mV, respectively (Fig. [2\)](#page-5-0). The sea bottom sediments at st. 16 contained a large amount of decomposed organic matter and a strong odor of hydrogen sulfide. It was also noted at st. 20. Most of the bottom sediments of the Crimean Black Sea coast had oxidizing environmental conditions:  $Eh = +82$  ...  $+210$  mV. The exception was st. 5 with slightly reducing medium conditions ( $Eh = +3$  mV) near cape Tarkhankut, which is typical of this region according to data (Mironov et al. [1992\)](#page-12-6). The bottom sediments of the Sea of Azov had slightly reducing environmental conditions (Eh =  $+1$  ...  $+44$  mV), with the exception of st. 16. These conditions enhance accumulation of hydrocarbons, because when redox potential of the medium is low, the bitumen transformation slows down.

It is known that Eh depends on pH. To obtain comparable data in the studied bottom sediments with different pH values, we calculated the hydrogen potential index (Fig. [3\)](#page-5-1) using the Clark equation (rH<sub>2</sub> = Eh/29 + 2pH) (Ganzhara [2001\)](#page-11-2). This index allows to compare different sediments considering Eh and pH values simultaneously.



<span id="page-5-0"></span>**Fig. 2** Physicochemical pH and Eh parameters in the sea bottom sediments (Tikhonova et al. [2016\)](#page-12-5)



<span id="page-5-1"></span>Fig. 3 Indicator rH<sub>2</sub>of the bottom sediment in the different parts of Crimea peninsula coast (Tikhonova et al. [2016\)](#page-12-5). I—oxidation processes, II—predominantly oxidation processes, III predominantly reduction processes, IV—reduction processes

According to scale described in (Ganzhara  $2001$ ), when  $rH_2$  is above 27, oxidative processes prevail, when it equals 22–25 - reducing, and below 20 - intense reducing. In our case, this indicator did not exceed 27, which indicates a low level of predominating oxidative processes. Reducing reaction was characteristic of the bottom sediments at st. 7. At other stations, with  $rH<sub>2</sub> < 20$ , intensive reductive processes occurred (Fig. [3\)](#page-5-1).



<span id="page-6-0"></span>**Fig. 4** EOM concentration in the different parts of Crimea peninsula coast (Tikhonova et al. [2016\)](#page-12-5).

Concentration of EOM detected in the Black Sea region bottom sediments was 10 –110 mg/100 g (Fig. [4\)](#page-6-0). Near the cape Ai-Todor the minimum values were noted, and the maximum—at the deep-water st. 20 and near the Yalta sewage pipe (st. 21). These values were very close and amounted to 110 and 106 mg/100 g respectively. The obtained indicators (Mironov et al. [1986\)](#page-12-4) referred to the III level of pollution, although they are close to its lower bound. However, this demonstrates the input of allochthonous hydrocarbons in the studied water area. At the same time, according to the department of marine sanitary hydrobiology (DMSH) of the Institute of Marine Biological Research (IMBR) data, the content of TPC at st. 20 was close to 0. It was in the open sea where wave mixing predominates and marine environment may become unrepresentative for this analysis under some weather conditions. Concerning the water area near the sewage pipe, the OH were found both in the bottom and in the surface water layers. Their concentration was lower than the MPC. Thus, we can suggest the presence of an TPC source in this area. Increased concentrations of EOM were noted in the bottom sediments of the Sea of Azov. They reached 187 mg/100 g. High values were also found at st.  $15(72 \text{ mg}/100 \text{ g})$  at the entrance to the Kerch Strait from the Black Sea. A high level of anthropogenic load can explain these indicators.

Compare the obtained data with these of the past years. Concentrations of EOM in the bottom sediments along the coast of the Crimea were typical of the region (Mironov et al. [1992\)](#page-12-6). However, at st. 12 near Karadag, it was 11 to 14 mg/100 g, while we registered 16 mg/100 g. That is, relative to 1976, levels of EOM are elevated. In general, sea bottom sediments were not contaminated with oil products.

For the bottom sediments of the Sea of Azov, the highest recorded values  $(187 \text{ mg}/100 \text{ g})$  equaled to those obtained by us in 2010 (186 mg/100 g) (Yurovskiy et al. [2012\)](#page-12-7). In general, the concentrations of EOM did not exceed the previously noted and inherent for the studied area (for shell rocks—20 mg/100 g, for pelitic silts - up to 230 mg/100 g) (Mironov [1996\)](#page-12-8). The data obtained on the characteristics of the sea bottom sediments corresponded to the previously described results and could be called natural-pure (Krylenko and Krylenko [2013;](#page-12-9) Tikhonova and Guseva [2012\)](#page-12-10).



<span id="page-7-0"></span>**Fig. 5** The TPC concentration in the different parts of Crimea peninsula coast (Tikhonova et al. [2016\)](#page-12-5).

Oil pollution was minimal in the Black and Azov Seas. At most stations, trace amounts were noted (up to 5 mg/100 g) (Fig. [5\)](#page-7-0). Earlier (2010) in the bottom sediments of the Azov Sea, these figures were noted in 65% of samples (Yurovskiy et al. [2012\)](#page-12-7), whereas at present we have noted concentrations higher than trace values in all samples. However, the obtained results are typical for clean and slightly polluted waters of the Black Sea.

The highest values of TPC were found at st. 15 (10.3 mg/100 g) near the entrance to the Kerch Straitand at st. 16 (10.2 mg/100 g), Azov Sea, which was natural for this shipping area. Earlier, from 2007 to 2010 (Yurovskiy et al. [2012\)](#page-12-7) there was a slight decrease in the content of EOM and TPC. In 2016 we obtained higher values of these indicators. In the Black Sea part of the Kerch Strait, the content of EOM was 72 mg/100 g, whereas in 2010 only 30.2 mg/100 g; TPC—10.3 mg/100 g, and in 2010—3.4 mg/100 g. That is, the recorded concentrations of EOM and TPC were 3 times higher compared to the data of 2010. This indicates contemporary processes of oil pollution accumulation associated with constant effluence of petroleum products in the strait and pre-strait zone.

The TPC percentage (Fig. [6\)](#page-7-1) of EOM ranged from 1 to 31%. The largest share



<span id="page-7-1"></span>**Fig. 6** The TPC percentage of EOM (Tikhonova et al. [2016\)](#page-12-5)

of TPC was noted at st. 5 and st. 7, which indicates the anthropogenic origin of hydrocarbons. This was confirmed by the data on the TPC concentration in the surface layer (data of DMSH IMBI) – in the areas of nature protection the maximum permitted concentration of oil products in the water was outmatched. For example, this phenomenon was registered in the water area of cape Tarkhankut and in the area of cape Aya. In the water areas of other reserves and wildlife sanctuaries, trace values of TPC were recorded. It should be noted that in the bottom sediments of the Azov Sea region, the TPC and EOM ratio was the same at all the stations and amounted to 6%.

Correlation dependence  $(r = 0.5)$  between the contents of EOM and TPC in the studied region was weak. When their concentrations are high, e.g. in the sediments of ports, this dependence is stronger (Rubcova et al. [2013\)](#page-12-11).

Thus, the obtained data on the content of EOM and TPC as well as physical and chemical features of the bottom sediments suggest that at present (2016) the properties of bottom sediments off the Southern Coast of the Crimea are typical of marine soils of the study region. It indicates the well-being of the study area as a whole. The bottom sediments in the Black Sea were less polluted with organic substances (level I-II) than in the Sea of Azov (level III). The exceptions in the Black Sea were at the deep-water st. 20 and st. 21 near the Yalta city sewage pipe. At the same time, the obtained values of EOM were at the lower boundary of level III. In general, there was a tendency to a gradual increase in EOM near the Black Sea coast, but the bottom sediments were not contaminated with oil products.

High concentrations of pollutants indicate the entry and existence of anthropogenic pollutants into silt bottom sediments with admixture of detritus. The maximum values of such trace elements as zinc, nickel, cobalt and chromium were found in the shallow water st. 16 in the Sea of Azov, where the sea soil was represented by silts with a large amount of EOM. The maximum content of Zn (195 mg/kg) in the bottom sediments exceeded its average value (140 mg/kg) at the shelf (Mitropolskiy et al. [1982\)](#page-12-3). Earlier (Kotelyanets and Konovalov [2012\)](#page-12-12), the content of this element in the area of the pre-strait zone of the Kerch Strait (st. 15) was 90 mg/kg, whereas in 2016 it was almost 2 times less (51.2 mg/kg). Zinc is a "universal pollutant", which is a part of the technogenic streams of almost all sources (Emelyanov et al. 2004), so it was recorded throughout this anthropogenically-loaded water area (Surova and Kuznecova [2002;](#page-12-13) Sovga et al. [2008\)](#page-12-14). According to the authors (Kotelyanets and Konovalov [2012\)](#page-12-12), the minimum Zn content in the Kerch water area increased 1.5 times compare to 2005, although its maximum content in 2007 and 2008 did not exceed the 2005 values. That is, this element is distributed unevenly in the study area. In the Black Sea, an excess of Zn content was recorded in the bottom sediments of the shelf at st. 7 while at the other stations the average concentration was 73.97 mg/kg, which was almost 2 times smaller.

At 100% of the stations in the Sea of Azov, the Ni content exceeded (with a maximum value at st. of 16–54.41 mg/kg) the average concentrations in the sediments of the shelf (42 mg/kg) (Emelyanov et al. 2004). Nickel can accumulate in the bottom sediments, in the immediate vicinity of the main sources of input. Accumulation of Ni in bottom sediments, especially at the coastal zone, correlates with the activity

of industrial and domestic sources of pollution (Nikanorov [1989\)](#page-12-15). In the Black Sea, this indicator was exceeded at 36% of the stations, with the highest values at st. 7 (46 mg/kg) and st. 21 (49 mg/kg). At the pre-strait st. 15, there was some decrease in the content of both nickel and zinc (25 mg/kg versus 37 mg/kg) (Kotelyanets and Konovalov [2012\)](#page-12-12). A weak dependence was noted between the concentrations of zinc and nickel in bottom sediments and EOM  $(r = 0.5)$ .

Cobalt concentrations at all the coastal stations exceeded the average values at the shelf—14 mg/kg (Mitropolskiy et al. [1982\)](#page-12-3). The content of Co in the upper layer of bottom sediments is quite high at st. 7 (165 mg/kg), and st. 8 (122 mg/g). Its highest content (300 mg/kg) was determined at st. 16, which was 21 times higher than its average value.

Distributions of chromium and cobalt were similar. They exceeded the average shelf values (45–90 mg/kg) at all stations, except for the Black Sea st. 2, where its concentration was close to the upper limit of standard values (84 mg/kg). Usually, an increase in the Cr content is characteristic of ports and berthing areas (Emelyanov et al. 2004). The maximum chromium content (260 mg/kg) was determined at st. 16. The highest concentration of this metal exceeded the approximate maximum permitted concentration by almost 2.5 times.

Elevated concentrations of vanadium were mainly confined to the coastal areas. Almost at all stations, except for st. 2, the V content exceeded the values at the Black Sea shelf (Mitropolskiy et al. [1982\)](#page-12-3). The highest concentration in the Sea of Azov was noted at st. 16 (421.3 mg/kg), and in Black Sea at st. 7 (324.7 mg/kg).

According to (Mitropolskiy et al. [1982\)](#page-12-3), arsenic level in the upper layer of sediments in the Black Sea was 0–130.4 mg/kg. The data obtained correspond to these values, but the lower limit was slightly higher—8.6 mg/kg. The average values in the Black Sea were higher than in the Azov Sea—55.4 and 42.2 mg/kg, respectively. At the same time, at st. 2, 12, 18 As concentration was below the detection limit by the X-ray fluorescence method (<20 mg/kg). According to (Perelman [1989\)](#page-12-16), the arsenics Clarke number is 1 mg/kg, so the samples of bottom sediments in the Crimean region can be considered rich in this element, with the exception of st. 2, 12, 18.

Concentration of strontium in the Black Sea sediments ranged from 200 (st. 2) to 647.4 (st. 8) mg/kg, with the exception of st. 15 where the highest content of 3085 mg/kg was noted. It is most likely related to sediments grain size distribution (Lukyanov et al. [2011\)](#page-12-17). The values higher than the Clarke number of 510 mg/kg (Perelman [1989\)](#page-12-16) were noted at 36% of stations in the Black Sea, whereas in the Azov region they did not exceed it at 100% stations.

Lead concentration in the bottom sediments was below the detection limit by the X-ray fluorescence method (Methods… [2002\)](#page-12-2). However, its minimal concentrations were found in the area of the Karadag nature reserve. According to the authors (Tikhonova et al. [2015\)](#page-12-18), in 2000 an excess of lead concentration was registered in water samples from the sources of Gyaur-Cheshme in the Valley of Roses (Karadag nature reserve), as well as in samples of well water at the Karadag biostation. It was more than 10 MPS (MPS =  $0.1$  mg/l). However, sampling in fresh and marine waters

in 2001 did not reveal it. This demonstrates that the source of Pb was non-permanent. Despite this type of pollution, at present, Karadag, was characterized by plenitude and biodiversity of bottom aquatic organisms (Kiseleva et al. [2002\)](#page-12-19) in comparison with other areas of the Black Sea.

The average levelof Mn in the sea bottom sediments of the Black Sea coast was 0.04%, the maximum (0.06%) was determined at the deep-water st. 20. In the Azov Sea it was 0.07% with a maximum of 0.08% at st. 18. Concentration of this element was much less than its background values in the studied region (Mitropolskiy et al. [1982\)](#page-12-3).

The spatial distribution of Ti and Fe was characterized by minimal concentrations in the Kalamitsky Bay (st. 2) and elevated values in the coastal waters near cape Ayia (st. 7), the pre-strait zone of the Black Sea (st. 15) and the Azov Sea (st. 16). The average Ti content in the Black Sea was 0.98%. The maximum (1.6%, st. 7) was 39% higher than the average, which was exceeded at 36% of stations. In the Sea of Azov, the concentration of Ti at all the stations was above its content in the sediments of the shelf. The Fe content in the Sea of Azov, as well as Ti, exceeded the limit values. In the Black Sea, these figures were slightly lower. Compare titanium oxides concentrations with the Clarke number of titanium in the earth crust (0.56%) (Chertko and Chertko [2008\)](#page-11-3), the content of titanium oxides in marine soils at all stations was higher. Titanium accumulates mainly with iron and the correlation between  $TiO<sub>2</sub>$  and Fe<sub>2</sub>O<sub>3</sub> was strong ( $r = 0.97$ ).

A number of factors define the processes of HM accumulation in sea bottom sediments; their intensity depends on their chemical composition, particle size distribution, pH, Eh etc. The ratio of redox processes is one of the major factors. However, our analysis of the dependence of HM concentration in marine sediments and the pH, did not reveal a correlation ( $r < -0.4$ ), whereas for EOM the inverse relationship was noted ( $r = -0.75$ ). At the same time, at stations with the highest concentrations of HM, different parameters of Eh were noted (st. 7 in the Black Sea and st. 16 in the Azov). At the deep-water st. 20 such phenomenon was not traceable.

According to data (Ramamurti [1987\)](#page-12-20) one can single out compounds in which HM are related in bottom sediments. For example, the main reserves of zinc are associated with iron and manganese oxides. According to (Papina [2001\)](#page-12-21), the main way of HM accumulation in sea bottom sediments is their co-sedimentation with iron and manganese hydroxides.

In general, HM values in the Sea of Azov at most stations exceeded those in the Black Sea. In the latter, the degree of soil contamination stood out at st. 7, in the Sea of Azov at st. 16. It was natural for the Sea of Azov, taking into account the level of anthropogenic load and natural conditions (shallow depth, particle size distribution, etc.), but for the water near cape Aya, a nature reserve, it was unusual. Apparently, an increase in content of heavy metals in bottom sediments was associated with technogenic pollution near Cape Aya caused by the submarine discharge of polluted ground waters (Yurovskiy et al. [2012\)](#page-12-7). The approximate total flux rate of these sources is 1915 m<sup>3</sup>/day (Ivanov et al. [2008\)](#page-11-4). In these water areas, geochemical barriers occur,

which contribute to accumulation of toxic substances in the "water - bottom" system. Examples of such accumulation of heavy metals in bottom sediments are known near the Long Island (United States) (Yurovskiy et al. [2012\)](#page-12-7).

## **5 Conclusions**

- 1. The bottom sediments of the open Crimean Black Sea coast, in relation to the content of EOM and physicochemical parameters, had properties typical of marine bottom sediments in this region. This indicated general well-being of the investigated areas. The bottom sediments in the Black Sea had levels I-II of pollution (according to concentration of EOM). The exception was the deepwater station and station near the Yalta sewage pipe, while the values obtained were at the lower boundary of level III. The Azov Sea was characterized by level III. There was a tendency to a gradual increase of EOM near the Black Sea coast, but the bottom sediments were not polluted with oil products.
- 2. The content of HM varied in wide ranges, and the zones with high values were not always close to the source of pollution.
- 3. At most stations in the Azov Sea, the HM concentrations were above those in the Black Sea, in particular, their maximum content was recorded at st. 16. Concentrations of Zn, Co and Cr, V (except for st. 2) exceed their natural content in the sediments of the shelf in all the studied areas. Ni concentration in the Azov Sea exceed Clarke number, which indicates the anthropogenic pollution sources.

The work was performed as part of the state assignment, of IBSS on the theme "Molismological and biogeochemical foundations of the marine ecosystems homeostasis" (№ AAAA-A18-118020890090-2). And MHI "Comprehensive interdisciplinary research of oceanological processes that determine the functioning and evolution of ecosystems of the coastal zones of the Black and Azov seas" (№0827-2019-0004).

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