Accumulation of oil products and heavy metals in bottom sediments at Temryuk harbor (the Sea of Azov, 2006-2020)

I Yu Matasova¹, V F Teyubova¹, O V Tsepordei²

¹Branch of Kuban State University – Novorossiysk Educational and Research Marine Biological Center, 43, Admiral Serebryakov Embankment st., Novorossiysk, 353905, Russian Federation
²Department of Foreign Languages, State Maritime University named after Admiral Ushakov, 93, Lenin Ave., Novorossiysk, 353924, Russian Federation

E-mail: semigorie@mail.ru

Abstract. The paper presents the results attained on the rate of accumulation as well as seasonal and inter-annual time profiles of oil products and some heavy metals (Cu, Zn, Pb, Fe) in the bottom sediments within the Temryuk harbor area (Gazovikov Bay) in the period from 2006 to 2020 when concentrations of oil products (OP) were recorded to vary from 88 to 413, copper – 13.6-116.0, zinc – 58.2-415.0, lead – 14.0-55.3 and iron – 8.4-41.0 g/kg, with median values of 211, 39, 122, 20 mg/kg and 30 g/kg, respectively. There is a trend for a higher rate of accumulation of oil products and lead. The paper specifies some geochemical features of bottom sediments at the seaport of Temryuk against the sediments in the Azov Sea. It delineates statistically significant relationships between levels of the pollutants under consideration, which decrease (as the correlation coefficient decreases) in the following sequence Cu-Zn> Cu-Pb> Zn-Pb >> Cu-Fe> Zn-OP> Zn-Fe, Cu-OP.

1. Introduction
Temryuk harbor is located in the southern part of the Temryuk Bay of the Azov Sea. An approach channel leads to the harbor. Within the harbor area, services are provided for transshipment of general, liquid (liquefied hydrocarbon gases and chemical cargo) and bulk cargo. The seaport has been developing existing terminals and is planning to build new ones (a transshipment complex for liquefied hydrocarbon gases, a transshipment complex for liquid chemical products, a terminal for transshipment of oil products, etc.).

A growing man-induced impact in harbor areas and, in particular, in the port of Temryuk, makes it more relevant to study the time course of pollutants accumulating in bottom sediments as in a depositing environment that can potentially become a secondary source of marine pollution. Yet, there are no published data on the accumulation of pollutants in the bottom sediments just outside the port of Temryuk. The paper aims to find out contents of heavy metals (Cu, Zn, Pb, Fe) and oil products in the soil just outside the Temryuk port, specify a seasonal and inter-annual rate of accumulation, establish certain geochemical features of harbor bottom sediments relative to those found to be present in the Sea of Azov, consider statistically significant relationships between concentrations of the studied pollutants.

The influx of pollutants to the water area can be related to both port detailing (corrosion of structural materials of ships and coastal structures, loss of cargo during transshipment, emergency
situations), and to some natural processes (input of terrigenous material with surface runoff, aerial travel, etc.).

One of the sources of the studied metals entering the harbor water area is the nearby agricultural land. Intensive agriculture enhances the destruction of organic matter, soil erosion, provokes an increase in the proportion of mobile forms of metals, as well as water-suspension removal from the landscape [1, 2].

The harbor area is located in a region with frontal attenuation of wind erosion and deposition of aeolian material referring to the so-called “eastern transport”. A geochemical spectrum of finely dispersed fraction (less than 0.1 mm) of the soil explored in the region showed it to be more than twice as enriched in zinc and copper relative to the larger fractions [3].

2. Materials and methods

Bottom sediments in the headwater area of the Temryuk port (Gazovikov Bay) were sampled at three stations on a quarterly basis (stage I – March, II – June, III – September, IV – December) in the period from 2006 to 2020 (Fig. 1).

Soil samples were taken using a Petersen dredger (sampling area 0.1 m²) from the surface horizon (0–25 cm), pointwise, in an amount of 1 kg. The samples of bottom sediments just outside Temryuk port were used to estimate concentrations of oil products, copper, zinc, lead and total iron. Chemical analysis of bottom sediments was carried out in the laboratory of Novorossiysk Educational and Research Marine Biological Center (branch) affiliated with Kuban State University.

The concentration of oil products was estimated by infrared spectroscopy on a KN-3 concentrator with an accuracy of 5–10%. The precision of analyses was 10%. The content of acid-soluble forms of copper, zinc and lead in bottom sediments were analyzed on a Shimadzu AA-7000F atomic absorption spectrometer with an error of 10%. The precision of analyses was 6–12%. The state standard samples of continental sedimentary deposits OOKO 202 and OOKO 203 (Russia) were used to control the accuracy of the results.

At present, maximum permissible concentrations for bottom sediments in the Russian Federation have not been established yet. Therefore, to assess the extent of pollution just outside the port of Temryuk with oil products and heavy metals, the authors used long-term average values of element concentrations in the Azov Sea bottom sediments, resulting from observations in 1996-2004. The following was also addressed: the granulometric composition of soil, which determines, among other things, the sorption capacity of deposits as long as pollutants are accumulated [4, 5].

Mathematical and statistical data processing was provided by Microsoft Office computer programs (Excel 2016), Statistica 6.0 software package.
Figure 1. Stations for sampling bottom sediments just outside the port of Temryuk.

3. Results and Discussion

The soil within the Temryuk harbor area is predominantly black, bluish-gray clayey silt with up to 3% fine gravel inclusions.

Oil products (OP). The concentration of oil products during the study period varied from 50 to 889.0 mg/kg, averaging 243.3±10.7 mg/kg. The maximum value was detected in June 2015, the minimum – in December 2006.

A seasonal time profile of oil products showed a tendency towards a decrease in bottom sediments during the calendar year (Table 1).

The time course of average annual oil products in the Gazovikov Bay sediments in the period 2006–2020 is characterized by a wave-like variability, with the maximum to be recorded in 2017, the minimum – in 2012. However, a general trend indicates an increase in soil pollution (Fig. 2). The trend is confirmed by the correlation dependence between a general array of oil products in soil and the year of sampling, which found the presence of a close relationship ($r=0.48$ at $\alpha=0.95$, $N=141$, $r_{crit}=0.17$).
Table 1. Average and median content of oil products and heavy metals in bottom sediments within Temryuk harbor (2006-2020)

| Index | Stage | Average for 2006-2020 | References |
|-------|-------|-----------------------|------------|
| OP, mg/kg | I | 267.8 ± 17.9 | 273.0 | 680-840 |
|       | II | 263.2 ± 27.4 | 231.3 | 35-46 |
|       | III | 229.1 ± 19.9 | 201.0 | 79-120 |
|       | IV | 206.4 ± 15.9 | 168 | 17.0-25.0 |
| Cu, mg/kg | I | 273 | 42.0 | 211.2 |
|       | II | 231 | 40.1 | 42.3 ± 1.9 |
|       | III | 201 | 39.4 | 40.7 ± 3.0 |
|       | IV | 168 | 37.5 | 39.4 |
| Zn, mg/kg | I | 200.5 ± 51.1 | 123.0 | 122.1 |
|       | II | 134.1 ± 8.8 | 121.0 | 39.4 |
|       | III | 129.5 ± 6.5 | 122.5 | 39.4 |
|       | IV | 131.2 ± 10.0 | 117.0 | 39.4 |
| Pb, mg/kg | I | 20.1 | 20.6 ± 2.1 | 117.0 |
|       | II | 20.1 ± 0.8 | 20.1 | 12.0 |
|       | III | 21.7 ± 1.3 | 19.9 | 19.9 |
|       | IV | 20.9 ± 1.6 | 21.2 | 20.8 ± 0.8 |
| Fe, g/kg | I | 30.7 ± 0.9 | 30.7 ± 0.9 | 29.5 ± 0.4 |
|       | II | 29.1 ± 0.6 | 29.4 | 29.5 ± 0.4 |
|       | III | 28.0 ± 1.1 | 29 | 29.6 |
|       | IV | 29.5 ± 1.0 | 29.2 | 26.2 |

Note: above the line is the arithmetic mean and error of the mean, below the line is the median.

Figure 2. Time course of oil pollution of bottom sediments just outside the port of Temryuk in the period 2006-2020.

Copper. Cu varied in the target soil in the range from 15.1 to 242 mg/kg, averaging 42.3 ± 1.9 mg/kg. The highest value was recorded in March 2006, the lowest – in March 2016. The fluctuations in average Cu concentrations in bottom sediments sampled at different stages showed no seasonal accumulation changes.

The time course of average annual Cu concentrations in the bottom sediments within the water area in the period under consideration is characterized by a wave-like variability with no pronounced trend for a decrease or increase in soil pollution (Fig. 3).

Zinc. During the study period, Zn ranged from 33.5 to 2060.0 mg/kg, with an average value of 150.8 ± 14.7 mg/kg. The highest concentrations were recorded in March 2006, the lowest – in June 2009. (Table 1). Seasonal accumulation of zinc in soil was not recorded.
The evolution of average annual Zn concentrations in the bottom sediments within the water area in the period under consideration is characterized by a wave-like variability with no pronounced trend (Fig. 4).

Figure 3. Time course of copper in bottom sediments just outside the port of Temryuk in the period 2006-2020.

Figure 4. Time course of zinc in bottom sediments just outside the port of Temryuk in the period 2006-2020.

Lead. Pb concentrations in the bottom sediments within the studied water area varied from 1.5 to 89.1 mg/kg, with an average value of 20.8 ± 0.8 mg/kg. The highest value was recorded in March 2006, the lowest – in March 2007. There is no seasonal Pb accumulation in soil (Table 1).

The time course of average annual Pb concentrations in the harbor sediments in the period 2006–2020 is characterized by a wave-like variability, but, generally, there is a high concentration of lead
(Fig. 5). This trend is confirmed by the correlation dependence between a general array of Pb concentrations in the soil and the year of sampling, which defined a close relationship \((r=0.23\) at \(\alpha=0.95, N=141, r_{crit}=0.17\)).

![Graph showing time course of lead in bottom sediments just outside the port of Temryuk in the period 2006-2020.](image)

**Figure 5.** Time course of lead in bottom sediments just outside the port of Temryuk in the period 2006-2020.

Iron. Fe concentrations in the soil considered ranged from 14.0 to 41.4 g/kg, with an average value of 29.5 ± 0.4 g/kg. The highest contents were recorded in March 2015, the lowest – in March 2016. There is no seasonal Fe accumulation in the soil (Table 1).

The time course of average annual Fe concentrations in the bottom sediments within the water area in the period under consideration is characterized by a wave-like variability with no pronounced trend (Fig. 6).

By way of comparing the factual findings with those for the Sea of Azov [3], the paper concluded that the average concentrations of the studied heavy metals in the bottom sediments within the Temryuk harbor were in the range of average values typical of the Sea of Azov (Table 1). The average concentrations of oil products were more than twice lower than those for the Sea of Azov. The trend in the level of oil pollution in bottom sediments just outside the Temryuk harbor in the period 2006–2020 (Fig. 2), showing an uneven increase in average concentrations of oil products, is different from that for the sediments of the Azov Sea. Thus, the data for 1985–2016 [6] indicate a decrease in soil pollution of the Sea of Azov with oil products on average from 1.0 to 0.4 g/kg. Comparable concentrations were attained by the researchers in 2019 [7-9].

Correlation analysis of the data set showed a significant relationship between the accumulations of a number of pollutants in the bottom sediments (Table 2).

A significant relationship between the pairs of pollutants was defined for bottom sediments within the port of Temryuk, allowing for the following series (in descending correlation coefficient): Cu-Zn> Cu-Pb> Zn-Pb >> Cu-Fe> Zn-OP> Zn-Fe, Cu-OP.

A correlation between chalcophilic elements (Cu, Zn, Pb) may be related to anoxic conditions in the bottom sediments of the Gazovikov Bay and their co-deposition as sulfides. Similar patterns were obtained for other sections of the Temryuk harbor [10]. Indirect confirmation of a reducing environment being formed in the soil of the considered water area is its color and odor (black silts with a “gley” odour). Moreover, during warm periods, NERMBC recorded viable spores of sulfate-reducing bacteria in the surface water layers of the studied water area.
**Figure 6.** Time course of iron in bottom sediments just outside the port of Temryuk in the period 2006-2020.

**Table 2.** Results of correlation analysis for bottom sediments at Temryuk harbor

| Index | Correlation coefficient ($\alpha=0.95$, $N=141$, $r_{crit}=0.17$) |
|-------|----------------------|
|       | OP       | Cu     | Zn     | Pb     |
| Cu    | 0.19     | 0.68   |        |        |
| Zn    | 0.21     | 0.52   | 0.46   |        |
| Pb    | 0.15     | 0.26   | 0.19   | 0.11   |
| Fe    | 0.12     |        |        |        |

### 4. Conclusions

The studies served to define the time course of oil products and a number of heavy metals (Cu, Zn, Pb, Fe) in the bottom sediments just outside the Temryuk harbor (Gazovikov Bay) in 2006-2020. The concentrations of oil products in the soil varied in the range from 88 to 413, copper – 13.6-116.0, zinc – 58.2-415.0, lead – 14.0-55.3 mg/kg and iron – 8.4-41.0 g/kg, with median values of 211, 39, 122, 20 mg/kg and 30 g/kg, respectively.

The long-term evolution of the studied pollutants shows a trend towards an increase in the amount of oil products and lead in sediments.

The average concentrations of Cu, Pb, Zn and Fe in the sediments at the Temryuk port during the observation period were within or slightly above the range of mean values characteristic of the Sea of Azov. The average concentration of oil products is 3 or more times lower than that for the Sea of Azov.

A significant relationship was defined between some of the target pollutants, which allowed the following series to be drawn in descending correlation coefficient: Cu-Zn > Cu-Pb > Zn-Pb >> Cu-Fe > Zn-OP > Zn-Fe, Cu-OP for the bottom sediments in the water area.

A correlation defined in the vapors of Cu-Zn, Zn-Pb, and Cu-Pb suggests that the deposition and accumulation of copper, lead and zinc in the bottom sediments at the Gazovikov Bay is to a certain extent their co-precipitation in the form of sulfides under anoxic water conditions.
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