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Organic Matter of the Bottom Sediments of the Ca Gau and Long Tau Rivers in the Can Gio Biosphere Reserve (Vietnam)

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Abstract

The purpose of the work is to assess the level of organic substances, including oil hydrocarbons, and the effect of water dynamics on the content of these substances in the bottom sediments of the river – sea contact zone of the Ca Gau and Long Tau Rivers located on the territory of the buffer zone of the Can Gio Biosphere Reserve (Vietnam, Southeast Asia). The following indicators of the ecological well-being of the water area were identified: physical-chemical indicators of water (pH, eH, salinity, temperature), concentration of chloroform-extractable substances and oil hydrocarbons in bottom sediments. Determination of chloroform-extractable substances in bottom sediments was carried out by the gravimetric method, oil hydrocarbons were determined by infrared spectrometry. The measurements were carried out on an FSM-1201 spectrophotometer. In the bottom sediments of the river Ca Gau and Long Tau, the recorded concentrations of chloroform-extractable compounds (from 54 to 90 mg/100 g) and oil hydrocarbons (from 9.6 to 13.8 mg/100 g) were close to trace levels. The study of some rivers of the Can Gio Reserve showed that this water area can be characterized as relatively safe in terms of the determined parameters. As a result of active water circulation in estuarine areas of rivers flowing in mangroves, physical-chemical characteristics of the environment underwent significant changes during the high tide: increase in salinity (by 1–5 PSU) and pH (by 0.24–0.31 units on average), and decrease in redox potential (by 9–18 mV). However, no close correlation between the changes in physical-chemical characteristics of the environment and the content of organic substances was revealed. This phenomenon is probably associated with the movement of bottom sediments and is only significant for chloroform-extractable substances in the estuarine part of the Long Tau River.

Keywords: river bottom sediments, chloroform-extractable substances, oil hydrocarbons, Can Gio Biosphere Reserve, Vietnam

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Органическое вещество донных наносов рек Кагау и Лонгтау в биосферном заповеднике Канзё (Вьетнам)

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Аннотация

Цель работы – оценка уровня содержания органических веществ, в том числе нефтяных, и влияния динамики вод на содержание данных веществ в донных наносах контактной зоны река – море рек Кагау и Лонгтау, расположенных на территории буферной зоны биосферного заповедника Канзё (Вьетнам, Юго-Восточная Азия). В качестве показателей экологического благополучия акватории были выбраны: физико-химические показатели воды (pH, Eh, соленость, температура), концентрация хлороформ-экстрагируемых веществ и нефтяных углеводородов в донных наносах. Определение хлороформ-экстрагируемых веществ в донных отложениях проводили весовым методом, нефтяных углеводородов – методом инфракрасной спектрометрии. Измерение проводили на спектрофотометре «ФСМ-1201». В донных наносах рек Кагау и Лонгтау зафиксированные концентрации хлороформ-экстрагируемых соединений (от 54 до 90 мг/100 г) и нефтяных углеводородов (от 9.6 до 13.8 мг/100 г) близки к следовым количествам. Проведенное исследование рек заповедника Канзё показало, что по определяемым параметрам данную акваторию можно характеризовать как относительно благополучную. В результате активной циркуляции вод в эстуарных районах рек, протекающих в мангровых зарослях, в период прилива происходят существенные изменения физико-химических показателей среды: рост солености (на 1–5 епс), повышение показателей pH (в среднем на 0.24–0.31 ед.), снижение окислительно-восстановительного потенциала (на 9–18 мВ). Однако тесной зависимости изменения физико-химических характеристик среды от содержания органических веществ не выявлено. Данное явление, вероятно, связано с перемещением донных наносов и носит достоверный характер только для хлороформ-экстрагируемых веществ в эстуарной части р. Лонгтау.

Ключевые слова: речные донные отложения, хлороформ-экстрагируемые вещества, нефтяные углеводороды, биосферный заповедник Канзё, Вьетнам

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Introduction

Can Gio Nature Reserve (Vietnam, Southeast Asia) acquired a biosphere reserve status in 2000. It includes mangrove forests southeast of Ho Chi Minh City. These forests are the green lungs of the country's biggest industrial city and harbour some of the largest diversity of mangrove plant species, invertebrates living in the thicket, and associated fishes and mollusks (URL: https://en.unesco.org/biosphere/aspac/can-gio).

The Can Gio region has a subequatorial tropical monsoon climate with two distinct seasons: the rainy season from May to October and the dry season from November to April with an average temperature of 25–29°C [1].

The total area of the Reserve is 757.4 km². It is divided into three key areas: the major area of 47.21 km², the buffer area of 411.39 km² (of which 38 km² is water area), and the transition area of 298.8 km² (of which 5.7 km² is water area). There are no settlements in the major and buffer zones. Shrimp fishing is carried out in some channels. Today, people living in the transition area (about 70,000 people) produce an additional pressure on the Reserve. Previously, in 1997, 54,000 people lived there, and before the Reserve was opened, in total 58,000 people lived in the area. Nowadays, the main fields of activity for the local population are agriculture and water management, fishing, salt mining and tourism.

The proximity of Ho Chi Minh City, the largest industrial city in Vietnam, cannot but affect the environmental situation in the protected area. This provides the need to control pollutants in the components of the Reserve's ecosystem.

Different ecosystems are represented within the Reserve: mangrove forests (40 % of the area), salt and mud marshes, grassy marine area (45 %) and agricultural land (15 %). The Kan Gio mangrove forest grows on swampy soils formed by alluvial clay deposits of the Saigon and Ong Nai Rivers. In addition, there are many large estuaries (Long Tau, Ca Gau and other rivers) along the coast. The area of the rivers and canals is 22,161 hectares accounting for 31.5 % of the Ho Chi Minh City area. Water from the East Sea enters the river system mainly at high tide. In the mixing zone, the most intensive processes of sedimentation of suspended solids brought by river water occur [1] and active accumulation of pollutants takes place [2].

At high tide, the movement of water masses transports surface bottom sediments. The nature of sediment movement depends on its physical characteristics (particle size distribution, particle density, hydraulic grain size etc.) and on the speed and depth of the water flow. In turn, various pollutants are actively accumulated in the bottom sediments. Tides are known to transfer particles up to 2 mm in diameter [3] with a predominance of particles up to 0.5 mm. It is this fraction of bottom sediments that can most actively accumulate organic molecules [4, 5]. Thus, it can be assumed that the content of organic compounds, including pollutants, in the downstream bottom sediments, in the river – sea contact zone, may to some extent alter the environmental indicators of the Reserve.

In that context, the aim of this work is to assess the levels of organic substances, including oil ones, and the impact of water dynamics on the content of those substances in the bottom sediments of the river – sea contact zone of the Ka Gau and Long Tau Rivers located within the buffer zone of Kan Gio Biosphere Reserve.

Materials and methods

The material for the study was sediment samples (0–2 cm) collected from the Ka Gau (Area 1: Stations 1.1, 1.2, 1.3) and Long Tau (Area 2: Stations 2.1, 2.2, 2.3) Rivers in the buffer zone of Kan Gio Biosphere Reserve (Fig. 1). In each area, river sediment was sampled at three points located across the riverbed: two nearshore points near the right and left banks and in the middle of the riverbed. The nature of the river sediment taken at Station 2.2 (mixture of sand and coarse pebbles) did not allow further chemical analysis. Samples were taken at two time periods: low tide (*R*) and high tide (*L*). Chemical-physical characteristics of water (pH, Eh, salinity) of the studied rivers were determined *in situ* with a Hanna HI9829 Multimeter by the staff of the environmental analysis laboratory of the Southern Branch of Joint Vietnam-Russia Tropical Science and Technology Research Center (JVRTSTRC). The temperature during the sampling period averaged 29.9 °C.

Determination of chloroform-extractable substances and petroleum hydrocarbons. Initial processing of sediment samples was carried out at the South Branch of JVRTSTRC by the staff of the IBSS Department of Radiological and Chemical Biology. Raw sediment samples were air dried, weighed and ground to a uniform dry mass, the sample was mixed and a subsample was taken for analysis. Further processing of the bottom sediments was carried out in the IBSS Chemoecological Laboratory. The resulting air-dry mixture (5 g) was extracted with chloroform until discolouration of the washing portions, the extracts were collected in a 100 ml conical flask, the solvent was distilled off in a water bath to a residual volume of 2–3 ml and transferred to weighing bottles. After evaporation of the chloroform, the weighing bottles were weighed and the weight of the chloroform-extractable substances (CES) in the test material was thus determined. After re-dissolving the CES in carbon tetrachloride, the mixture was applied to an aluminium oxide column for determination of oil hydrocarbons (OH) on a spectrophotometer

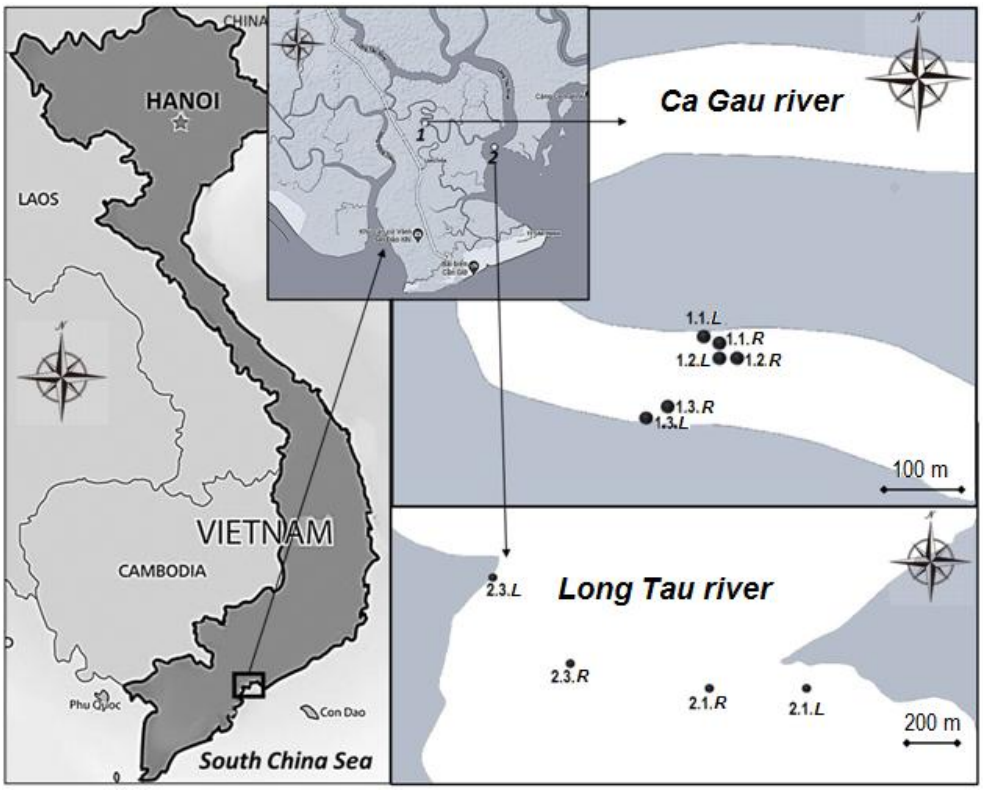

Fig. 1. Map of sampling bottom sediment stations in the Ca Gau and Long Tau rivers in the Can Gio Biosphere Reserve, May 2021 (*R* is for sampling stations at low tide, *L* – at high tide)

FSM-1201 [1), 2)]. CES and OH concentrations were converted to 100 g weight of air-dry weight of sediments. Correlation analysis ($p = 0.05$) was performed using a Microsoft Excel 2010 analysis package.

Results and discussion

Bottom sediment sampling stations (Areas 1, 2) are located in river reaches in the zone of tidal influence. Water dynamics impacted on changes in physical-chemical water parameters (Fig. 2). During the high tide, water salinity increased by 1 PSU in the water area of Area 1 and by 5 PSU in Area 2 located almost at the mouth of the Long Tau River. Salinity increase in the river water during high tides is natural and related to the inflow of saltier sea water. Following the salinity

[1)] Matveeva, I.S. and Ignatchenko, A.V., 2014. [*РД 52.10.803-2013. Weight Content of Petroleum Hydrocarbons in Marine Sediment Samples. Methodology for Measurements by Infrared Spectrometry*]. Moscow, 24 p. (in Russian).

[2)] Oradovskiy, S.G., ed., 1977. [*Guideline for Methods of Sea Water Chemical Analysis*]. Leningrad: Gidrometeoizdat, 118–131 p. (in Russian).

gradient, physical-chemical characteristics of water changed (Fig. 2): hydrogen ion concentration shifted towards alkalinity; redox potential slightly decreased. Redox potential slightly decreased. The decrease of Eh values (down to –40 mV) during the high tide is consistent with the increase of pH values (up to 7.58). This fact indicates an improvement in oxygen conditions when the seawater enters the river water in the studied wetlands [6]. The change in pH values (in Area 1 water area by 0.24 units on average and in Area 2 by 0.31 units) was more pronounced than the change in redox potential. Similar fluctuations in pH due to water movement within the tidal cycle were observed in other estuarine systems [7, 8]. Water temperature tended to increase during the high tide. At low tide, the mean value of surface water temperature was 29.5 °C in Area 1 and 29.9 °C in Area 2; at high tide it was 30.0 °C in Area 1 and 30.2 °C in Area 2. The tide was at night (9–10 p.m.), which may have been a factor in the decrease in surface water temperature. The tide was in the afternoon (around 3 p.m.), when the surface water could be warmed by the sun's rays. According to long-term satellite observations, the average sea water temperature off the coast of Kan Gio Reserve in May is 29.8°C, ranging from 28.6 to 31.0 °C (URL: https://www.seatemperature.org/asia/vietnam/cn-th-may.htm). The fact that the temperatures recorded at high tide are higher than

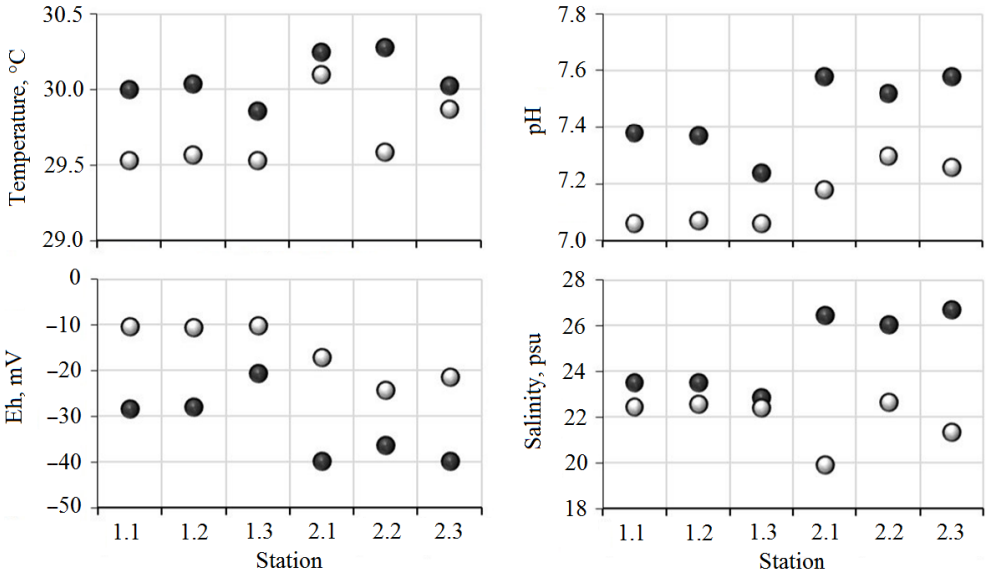

Fig. 2. Physico-chemical parameters of water at the bottom sediments sampling stations at low tide (●) and high tide (◍) in the Ca Gau and Long Tau rivers in the Can Gio Biosphere Reserve, May 2021

the long-term observations may indicate that the surface water warms up during the day, which was recorded during the survey.

Concentrations of CES in bottom sediments in the coastal water area of Kan Gio Reserve ranged from 54 mg/100 g to 90 mg/100 g (Fig. 3). The maximum values of CES in Area 1 were found at Station 1.3 *R* and the minimum values – at Station 1.2 *R*; in Area 2 – at Stations 2.3 *L* and 2.3 *R*, respectively. The increased content of CES in the bottom sediments of the Ka Gau River compared with that of the Long Tau River may be due to the fact that the first area is located in the depth of the river system and the second area is at the direct influx of the river into the sea where organic-rich river water is diluted with marine water. A similar phenomenon has also been observed by other authors, where an increased content of organic matter in river sediments has generally been observed mainly in the river basins in the central part of the mangroves compared to those in their estuarine sections [9].

It is known [10] that the most active processes of primary diagenesis of organic matter take place at the water – bottom interface, so the previously noted changing pH and Eh values of water, which directly influence the course of these processes, may influence the quantitative indicators of organic matter accumulated in bottom sediments and transported by tidal currents. However, no close correlation between the concentration of organic matter and physical-chemical indicators of water was observed, with the exception of a weak positive correlation for salinity ($r = 0.48$). Although in our case it is difficult to speak about the relationship between salinity and the studied components of organic matter, the literature [11] contains data on a significant inverse proportional relationship between the content of organic and inorganic matter and salinity [3)]. The influence of these factors is probably hard to detect due to their variability over a short period of time making it impossible to determine the specifics of sedimentation conditions.

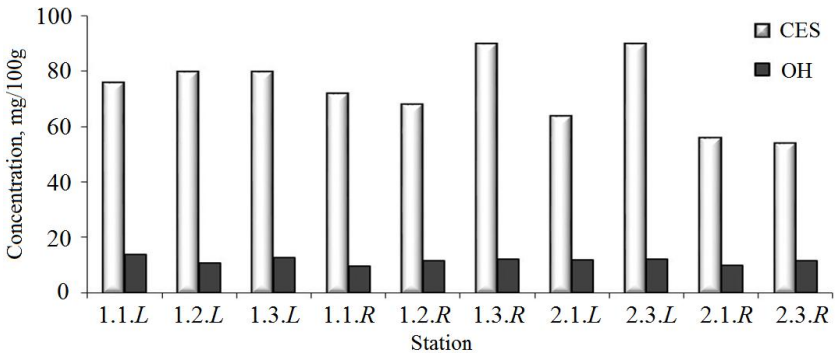

Fig. 3. CES and OH concentrations in bottom sediments of Ca Gau and Long Tau rivers in the Can Gio Biosphere Reserve, May 2021

[3)] Ovsepyan, A.E., 2007. [*Distribution, Migration and Transformation of Mercury in the Northern Dvina Estuary*]. Ph.D. Thesis. Rostov-on-Don, 178 p. (in Russian).

A comparison of CES levels in river sediments, the composition of which changes due to their active transport by sea water, indicated that the total CES content was decreasing during low tide. In Area 1 (deep in the Kan Gio Peninsula), this decrease was negligible, but in Area 2 (the estuarine part of the Long Tau River), it decreased by almost 30 %. This is probably due to the fact that estuarine areas are generally characterized by intense circulation [4)] and deposition [9] of various substances caused by water dynamics. A similar trend existed for OH but it was not significant. This is probably due to the low OH level and lack of significant differences in their content in both river and sea sediments.

There is a regional classification of levels of organic pollution in bottom sediments [12]:

- Level I – less than 50 mg/100 g;
- Level II – 50–100 mg/100 g;
- Level III – 100–500 mg/100 g;
- Level IV – 500–1000 mg/100 g;
- Level V, the most dangerous, – over 1,000 mg/100 g.

In accordance with this classification the values obtained in this study for the whole water area refer to pollution levels I–II, and the studied area can be classified as conditionally clean [13, 14]. These levels are comparable with similar indicators of coastal bottom sediments in other protected areas, in particular, the Kazantip Nature Reserve (North-Eastern Crimea) [15] and the Laspi Landscape Reserve (Southern Coast of Crimea) [16]. Recorded levels of organic matter are significantly lower than, e. g., in the estuarine part of the Yazna River, South-East Asia [17].

OH concentrations ranged from 9.6 mg/100 g to 13.8 mg/100 g (Fig. 3). If we compare the obtained results with the standards from Dutch Lists [5)], the values were rather low and only by 1.9–2.8 times exceeded the concentration threshold, at which the exposure under chronic pollution is insignificant (5 mg/100 g). The percentage of OH in CES ranged from 13 % to 21 %. The obtained values indicate a low level of oil contamination, and therefore the recorded hydrocarbons are of predominantly autochthonous origin.

Conclusion

The recorded concentrations of chloroform-extractable compounds (54–90 mg/100g) and oil hydrocarbons (9.6–13.8 mg/100g) in bottom sediments of the Ka Gau and Long Tau Rivers (the buffer zone of Kan Gio Biosphere Reserve)

[4)] Denisov, V.V., ed., 2004. [*Ecology. A College Textbook*]. Rostov: ITS MarT M, 672 p. (in Russian).

[5)] Available at: esdat.net/Environmental%20Standards/Dutch/annexS_I2000Dutch%20Environmental%20Standards.pdf (Accessed: 5 September 2022).

are close to trace levels. Consequently, the status of this component of the river ecosystems is favourable in terms of organic and oil pollution content. Active water circulation in estuarine areas of mangrove rivers at high tide results in significant changes in physical-chemical environmental indicators: salinity increase (by 1–5 eps), pH increase (on average by 0.24–0.31 units), redox potential decrease (by 9–18 mV). However, no close correlation was found between changes in the physical-chemical characteristics of the environment and the content of CES and OH. This phenomenon is probably associated with the movement of bottom sediments and is only significant for CES in the estuarine part of the Long Tau River. In other cases we can only speak of a trend.

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Olga V. Soloveva – analysis of the results obtained, discussion of the results, writing and formatting of the article

Nguyen Trong Hiep – sampling planning and sampling of bottom sediments, determination of physico-chemical parameters of water.

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