Hydrocarbon Composition Characteristics of River Bottom Sediments in the Region of High and Low Tides Influence (Exemplified by Ca Gau and Long Tau Rivers, Can Gio Biosphere Reserve, Vietnam)

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The aims of this study were assessment of levels and identification of possible sources of hydrocarbons in river sediments of “river-sea” contact zone of the Ca Gau and Long Tau rivers flowing through the territory of the Can Gio Biosphere Reserve (Vietnam, Southeast Asia) in different phases of the tidal cycle. Aliphatic hydrocarbons were detected using gas chromatography, polyaromatic substances - high performance liquid chromatography. In the Ca Gao riverbed, bottom sediments contained higher concentrations of aliphatic and polyaromatic hydrocarbons than in the mouth zone of the Long Tau River. In general, the recorded values of the hydrocarbon content were low and typical for slightly polluted water areas. The dominant source of aliphatic hydrocarbons in sediments of the studied water areas was terrestrial vegetation. Polyaromatic hydrocarbons probably entered the waters of the river in the upper sections of its watercourse, and, further, accumulated in bottom sediments. It is also possible that this class of substances entered with sea water brought in during the high tides.

1. INTRODUCTION

The state of the Can Gio region as a protected area was recognized internationally in 2000 by UNESCO. It is located in a coastal area south-east of Ho Chi Minh City, the main industrial center of Vietnam. Protective measures in the reserve create conditions for improving environmental protection in various habitats: from coastal areas to the borders of Ho Chi Minh agglomeration. The mangrove biotope located here is inhabited by a large number of living creatures [1, 2]. The Can Gio region has a subequatorial monsoon tropical climate. The period with a large amount of precipitation falls on May-October, with a small amount - in November-April, with temperature from 25 to 29° C [3].

With their special ecological conditions, the mangrove forests of Can Gio represent an intermediate ecosystem between aquatic and terrestrial, freshwater and marine ecosystems. A large amount of sediments from the Dong Nai and Saigon Rivers enters the forest, along with the influence of the neighboring Eastern Sea and tidal waves. Thus, the mangrove forest is not only "lungs", but also "kidneys" with their function of purifying the air and wastewaters of industrial cities on the stretch of the upper reaches of the Dong Nai and Saigon Rivers to the Eastern Sea. Mangroves help to reduce the damage caused by storms and floods by reducing the energy of wave impact by up to 50%.

The Can Gio reserve has a very typical coastline, about 20 km long, the so-called alluvial sea. There are many large estuaries along the coast, of such rivers as Long Tau, Ca Gau, etc. The area of rivers and canals is 22161 hectares, which covers 31.49% of Ho Chi Minh City area. Water from sea enters the river system, mainly through bays. In the mixing zone, the most intensive processes of sedimentation of suspended matter transported by the river waters [3] and the active accumulation of pollutants [4] occur.

With the movement of water masses within the tidal cycle, the transfer of entrained bottom sediments induced by the movement of water masses is inevitable. At the same time, the nature of the movement of sediments depends on their physical characteristics (size and shape, specific gravity, etc.), particle size distribution, for example, the speed and depth of the flow. Under natural conditions, different phases of sediment transport usually occur simultaneously, and to draw a clear boundary between them is impossible [5]. Tides are known to transfer particles to 2 mm in diameter [6], with predominant transportation of particles of 0.5 mm in diameter. Just that very fraction of bottom sediments is able to accumulate organic molecules most actively [7; 8]. Thus, it is likely to expect changes in

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the composition of long chain carbon compounds, including pollutants associated with river soil and suspended substance in interaction place of sea and river waters. The significance of such kind of transfer for the formation of pollution levels in the water body remains little studied.

Can Gio location in the river delta makes it a particularly sensitive area. This is due to the fact that rivers carry pollutants into the sea incoming from their banks, as well as a result of economic activities in them [9; 10; 11; 12], while a significant part of the pollutants is deposited in “river-sea” mixing zone [13].

Despite environmental, economic and social importance of mangrove forests they have been heavily damaged by different anthropogenic activities (aquaculture, harbors, many industrial facilities and other industries) mostly in the southern region of the Vietnam [14; 15]. Also they affected by sea level rising connected with chemical pollution, climate change and etc. [16; 17; 18]. As the result the reserve area is under the pollution by different substances, especially hydrocarbons, risks.

In view of the foregoing, the purposes of this study were: 1. assessment of the levels of hydrocarbons (HC) in river soil of “river-sea” mixing zone of the Ca Gau and Long Tau rivers flowing through the territory of the Can Gio protected area (Vietnam, Southeast Asia); 2. identification of possible origin of aliphatic hydrocarbons (AHC) and polycyclic aromatic hydrocarbons (PAHs); 3. assessment of effect of tidal cycle on the concentration and individual composition of HC (n-alkanes, PAHs) in zone of interaction between river and sea waters exemplified by the tropical rivers Ca Gau and Long Tau.

2. MATERIAL AND METHODS

The material for study were river sediments (0-2 cm) sampled by means of core column for collecting of bottom sediments in the two rivers – Ca Gau (station 1) and Long Tau (station 2) on territory of the Reserve in spring 2021 (Fig. 1). Samples were taken in two time periods: low tide (at low water level - R) and high tide (at high water level - L). Station 1 was far from the sea, in the inland area of the reserve on the Ca Gau River, and Station 2 was allocated on the Long Tau River, in the place adjacent to the sea. Sampled sediments were put into containers and placed to the boxes with ice to deliver to the laboratory. The chemical and physical characteristics of water (pH, Eh, salinity) at sampling stations on the rivers were determined *in situ* by means of multimeter Hanna HI9829.

Fig. 1. Map of river sediment sampling in the Ca Gau (A) and Long Tau (B) rivers (Can Gio Biosphere Reserve, 2021).

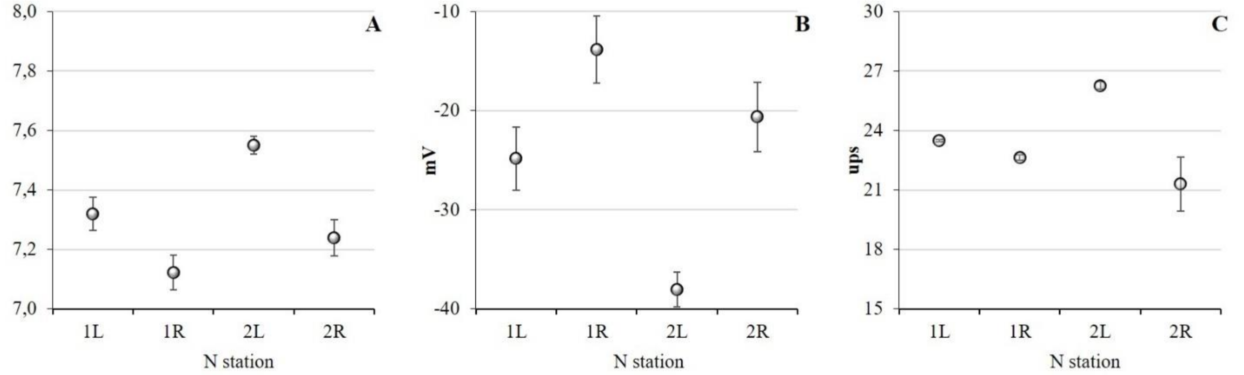

Fig. 2. Potential of hydrogen, Redox potential and Salinity of water in the studied rivers: A - pH, B - Eh, mV, C - salinity, psu, 2021.

Hydrocarbons and n-alkanes were determined in river sediments using the method of gas chromatography [19] by means of the Crystal 5000.2 chromatograph in IBSS Spectrometry and Chromatography Research Center. The concentration of PAHs was defined using high-performance liquid chromatography method (Federal Register 1.31.2007.03548) on an ECOM Beta-10US liquid chromatograph. To identify sources of hydrocarbons were used different indices and molecular ratios: TMD, TAR, ACL, LWH/HWH, C_{31}/C_{29}, C_{31}/C_{19}, CPI_1, CPI_2, Paq, NAR, Wax_{Cn}, Pr/Ph; C_{17}/Pr; C_{18}/Ph; R/UCM [20–31]. Data processing was carried out by applying Statistica 12 and Microsoft Excel.

3. RESULTS AND DISCUSSION

Both sampling stations were located at the river sites in the zone of tidal influence. The study of bottom sediments was carried out during high and low tide, forming two data arrays for each of the stations. The tidal amplitude in the sampling area in Station 2 is about 3 m, in Station 1 it is about 2 m [1; 32]. During the high tide, an increase in water salinity (difference between high tide phase salinity and low tide phase salinity) was noted at Station 1 by 1 psu, at Station. 2, located almost to the East Sea - by 5 psu. Following the salinity gradient, other characteristics of the water changed (Fig. 2): the pH value changed towards alkalization; redox potential decreased slightly.

3.1. Content and possible sources of n-alkanes

As we assumed the effect of river bottom soil transportation on the levels and content of HC in the river soil of the estuaries of the rivers, the study of the content and composition of n-alkanes was defined during low and high tides. The average concentration of aliphatic hydrocarbons (Fig. 3) in the bottom sediments at Station 1 was 40.30±13.91 µg/g during high tide and 42.07±6.78 µg/g during low tide. At Station 2 at high tide, the AHC concentration amounted to 26.15 µg/g; at low tide, it was 23.3±10.50 µg/g. At the same time, at low tide, 100% of HC were presented by aliphatic compounds (Fig. 3), while at high tide, an unresolved complex mixture could be seen on the chromatograms.

The mean content of AHC, as an environmental characteristic of the region at Station 1 in the river bottom soil of the Ca Gau River was 41.18±6.94 µg/g. At the outfall of the Long Tau River (at St. 2), this indicator was significantly lower (p_v=0.62) and equaled 22.60±6.10 µg/g.

The amount of n-alkanes at Station 1 was higher than at Station 2, and this difference did not depend on the phase of the tidal cycle. In general, the recorded HC levels may be considered low. In accordance with the standards proposed by the Dutch Lists [33], bottom sediments that are safe by this indicator, should contain no more than 50 µg/g. In the sediments of the rivers under study, in all cases, the average concentrations did not exceed those conditional values.

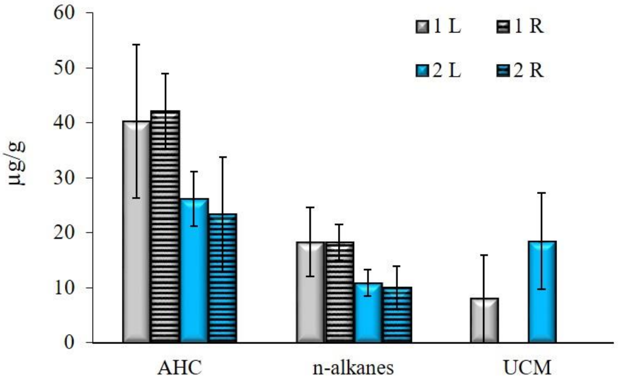

Fig. 3. The concentrations of aliphatic hydrocarbons, n-alkanes and the unresolved complex mixture of river soils of the Ca Gau (st.1) and Long Tau (st.2) rivers, 2021.

At both stations, n-alkanes were identified in the length range of hydrocarbon chains C_{17}–C_{34} (Fig. 4).

At Station 1, n-alkanes exhibited unimodal distribution, with a predominance of high-molecular compounds C_{29}–C_{31}. Long chain homologues of n-alkanes are predominantly of natural origin. Odd peaks prevalence is characteristic for terrestrial vegetation to [34]. Even n-alkanes with a high molecular weight (C_{28}, C_{30}, C_{32}) are often associated with sapropelic matter, which is formed due to the activity of unicellular hydrobionts, lower plants, and is autochthonous for aquatic ecosystems [34]. At Station 2, the distribution of homologues was relatively monotonous, with individual peaks, which may be a sign of the presence of petroleum hydrocarbons. At both stations during low tide, a significant increase in the content of hydrocarbon C_{24} was observed, its portion increased from 2-8% to 20-21%. The absolute content of this compound increased 3 times at Station 1, and 10 times at Station 2. The presence of n-alkane C_{24} in bottom sediments is usually associated with microbial activity [35; 36]. An increase in the content of n-alkanes of bacterial origin during low tide was observed in the estuaries of other rivers of the Far Eastern region [37]. At the same time, other peaks associated with bacterial activity (C_{18}-C_{22}) were not expressed significantly, which suggests that the increase in the content of the C_{24} homologue at low tide was most likely due to the influx of plant compounds [38; 39] from mangroves. At Station 2 where the gradient of salinity was larger, the change in the content of C_{24} was more intense. Probably, at low tide there was an active influx of fresh water from mangrove swamps that carried hydrocarbon compounds. The combination of several factors (influx of plant n-alkanes and bacterial activity) was likely to cause that phenomenon.

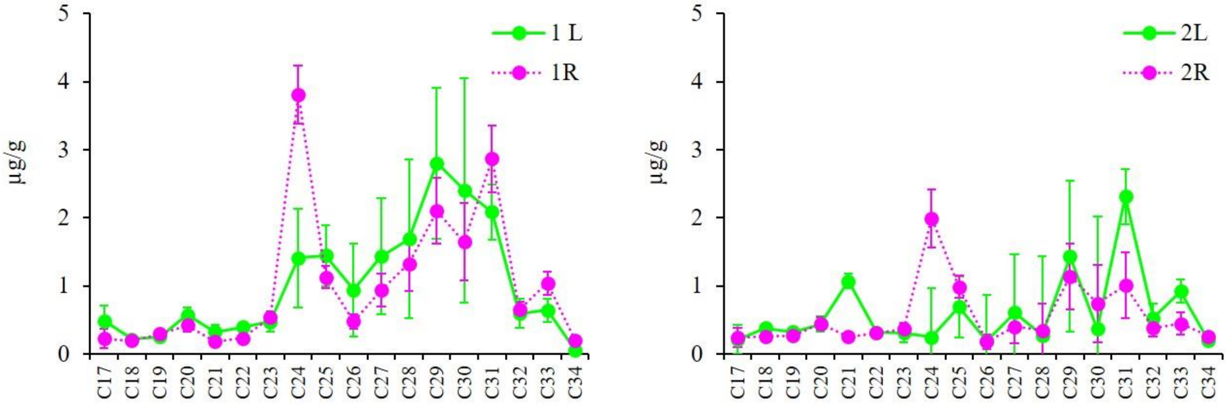

Fig. 4. Individual composition of n-alkanes (with standard error) of bottom sediments of the Ca Gau (st.1) and Long Tau (st.2) rivers, 2021

At Station 2, located closely to the East Sea, the proportion of C_{29}–C_{31} compounds associated with higher terrestrial vegetation, primarily, decreased during the low tide. This may be due to the transportation of bottom sediments by tidal waves from the seaward areas of the estuary. A similar phenomenon was practically not observed at Station 1, located at a greater distance from the place where the river flows into the sea, and, as a result, is less prone to the introduction of bottom soils from the lower seaward sections of the river.

According to the total AHC content, the bottom soils of the Ca Gau and Long Tau rivers can be also considered relatively clean [33]. However, to determine anthropogenic pollution as an important indicator of the conservation of the ecosystem of the reserve, it is necessary to assess not only the overall levels of hydrocarbon content, but also to establish the composition of hydrocarbons in the sediments under study [34]. In some cases, exceeding standard values for the content of hydrocarbons is a consequence of natural processes [40]. For a more reliable assessment of the sources of HC input, it is necessary to use molecular markers characterized by diagnostic functions.

The calculated markers of HC genesis can be divided into several groups (Table 1). Those that allow one to differentiate allochthonous and autochthonous compounds: TAR, Alkterr, TMD, ACL, LWH/HWH. Other biomarkers make it possible to clarify the biogenic nature of hydrocarbons, in particular, to assess the contribution of the arboreal and herbaceous components in the allochthonous substance, these are molecular markers C_{31}/C_{29}, C_{31}/C_{19}, ACL. To differentiate the oil and biogenic background, the following ratios are used: the carbon preference index (CPI), the unresolved complex mixture (UCM), its ratio to the amount of aliphatic hydrocarbons, ACL, LWH/HWH, Pr/Ph, C_{17}/Pr, C_{18}/Ph.

Table 1. Molecular marker meaning in bottom soils of the Ca Gau and Long Tau rivers, 2021

Index	**St. 1L**	**St. 1R**	**St. 2L**	**St. 2R**
ACL	28.93	29.44	29.74	28.61
TMD	5.23	6.41	4.42	3.40
NAR	0.10	-0.03	0.47	0.01
CPI_1	2.36	2.19	3.07	2.12
CPI_2	3.86	2.95	7.07	3.10
LWH/HWH	0.15	0.08	0.27	0.18
Paq	0.28	0.25	0.21	0.41
C_{31}/C_{19}	9.33	9.82	8.91	3.47
C_{31}/C_{29}	0.93	1.40	1.61	0.85
TAR	8.47	11.96	11.00	4.73
Wax	48.41	48.83	48.15	47.62
Pr/Ph	0.29	0.87	0.12	0.33
C_{17}/Pr	9.77	3.45	9.61	4.37
C_{18}/Ph	1.46	2.00	1.88	1.19
R/UCM	5.05	-	1.42	-

In calculating the terrestrial-marine index (TMD), the sum of C_{15}–C_{21} n-alkanes gives an idea of autochthonous compounds [21]. The sum of odd homologues C_{25}–C_{35} is predominantly presented by terrigenous alkanes [20]. The ratio of these groups makes it possible to identify origin of organic matter more reliably, at the same time, exclude influence of such factors as the particle size of solid river material and rate of sedimentation [22]. A high (>1) ratio characterizes the strong influence of terrigenous matter; with its decrease, one can judge about a decrease in its significance. In our case, the values of this index varied in the range of 3.40–6.41 (Table 1). The high content of specified groups of n-alkanes demonstrate a significant input of hydrocarbons from earth. This phenomenon seems to be natural, taking into account the mangroves growing on the banks of the studied rivers, and the cases previously described for the estuaries of other river systems [4].

Another parameter widely used to identify the source of hydrocarbons is the ratio of individual compounds with an odd number of atoms, the so-called TAR (terrigenous/aquatic ratio). This indicator varied 4.70–12.00. The indicated values of this coefficient characterize the predominance of allochthonous material of terrestrial origin [22].

The ratio ∑C21-/∑C22+ (LWH/HWH) used to assess the preferential pathway for organic matter. The components ∑C21- reflect autochthonous materials [21], while ∑C22+ shows terrigenous input [20]. At the sampling stations this ratio was in the range of 0.08–0.27, which demonstrates a significant terrigenous input.

Terrestrial vegetation plays an important role in the formation of the composition of HC (*correlation of n-alkanes*) in river sediments. The main peak associated with arboreal vegetation falls on C_{29}, while the peak reflecting herbaceous vegetation is associated mainly with C_{31} [27; 26]. The ratio of these parameters (C_{31}/C_{29}) varied in a wide range: 0.85–1.61. Thus, we can say that, in general, the contribution of both components was approximately the same.

The C_{31}/C_{19} ratio is an index showing the ratio of allochthonous and autochthonous fraction. It was 3.47–9.82, which indicates the predominance of allochthonous matter.

The average chain length (ACL) of n-alkanes is related to their origin. The hydrocarbons of timbered plants are characterized by low ACL values. Large ACLs indicate the dominance of herbaceous vegetation in HC formation [25]. When oil pollution is fresh, a decrease in ACL is also noted [41]. This parameter was 28.61–29.74 (the identical role of herbaceous and woody plants in the formation of organic matter). At the same time, it should be taken into account that this approach is strictly applicable only to “fresh” organic matter [34].

The moisture index (Paq) reflects the participation of terrestrial plants in the formation of organic matter [42; 43]. Its magnitudes from 0.21 to 0.41 indicate fresh HC input from macrophytes.

The proportion of plant waxes (Wax) makes it possible to estimate the relative contribution of the nutrient [44]. The values of this indicator were 47.62–48.83. High values of the Wax index demonstrate the predominant contribution of biogenic sources [45; 46].

The CPI index is widely used, which is the ratio of the number of n-alkanes with an odd and even number of carbon atoms [34; 44]. The n-alkane groups with short and long carbon chains generally have carbon preference index, which are designated CPI_1 and CPI_2, respectively. Calculations showed that for lighter n-alkanes, CPI_1 varied in the range of 2.12–3.07. The predominance of compounds with an odd number of carbon atoms for low molecular weight compounds may indicate not only the fresh supply of petroleum products, but also their production as a result of the activity of microorganisms and macrophytes [34; 47; 48]. Thus, it can be assumed that the n-alkanes with short carbon chains identified in the bottom sediments were predominantly of natural origin. The CPI_2 values describing the ratio for long-chain n-alkanes ranged from 2.95 to 7.07. All samples showed a predominance of odd compounds. In the high molecular weight region, the oddness indices were higher than in the low molecular weight region.

The Pr/Fy ratio is used to differentiate biogenic (>1) and anthropogenic hydrocarbons [46; 49; 50]. In the water bodies studied, its values were in the range of 0.12 – 0.87, i.e. in all cases they were less than 1, which indicates the presence of oil and oil products in the environment. Moreover, during high tide, the value of this index decreased. This points to an increase in the proportion of hydrocarbons of petroleum origin relative to biogenic in the mixture extracted from bottom sediments, taken at the time of high tide.

The ratios of iso-homologues (pristane and phytane) to normal hydrocabons, in particular C_{17}/Pr and C_{18}/Ph, allow one to determine the origin of hydrocarbons and estimate the rate of their biodegradation [51; 52]. Low values of these ratios (<1) indicate the presence of degraded oil. In the case of fresh oil input, the values of these reference indices exceed 1 [53]. The values of these ratios in all cases exceeded 1, which indicated the presence of fresh oil products in the bottom sediments. It should be noted that during high tide periods the C_{17}/Pr index increased by 2–3 times, which is probably due to the inflow of fresh oil during the tidal movement of water and bottom sediments.

UCM (Unresolved Complex Mixture) is a complex mixture of isomers and homologues, branched and cyclic hydrocarbons, the separation of which is impossible in a chromatographic column [54]. One of the most reliable criteria for the presence of HC biodegradation products is the presence in the samples of a chromatographically unseparated complex part of UCM with a maximum in the high molecular weight region [34]. The number of oil components in UCM can reach up to 250,000 compounds, which indicates that UCM is the most composite complex mixture of organic compounds that exists on Earth [55]. At the same time, despite the obvious connection with oil sources, the presence of UCM among low concentrations can also be associated with bacterial decomposition of autochthonous organic substances [56]. The configuration of the unresolved complex mixture background depends on its composition. The nature of the “hump” of natural and anthropogenic hydrocarbons differs [34]. Anthropogenic compounds are characterized by a "hump" in the macromolecular region. Such a maximum in the low-temperature region arises due to the microbial degradation of natural organic compounds, in particular, plant detritus [57]. In the mixing zone of the Long Tau and Ca Gau rivers,

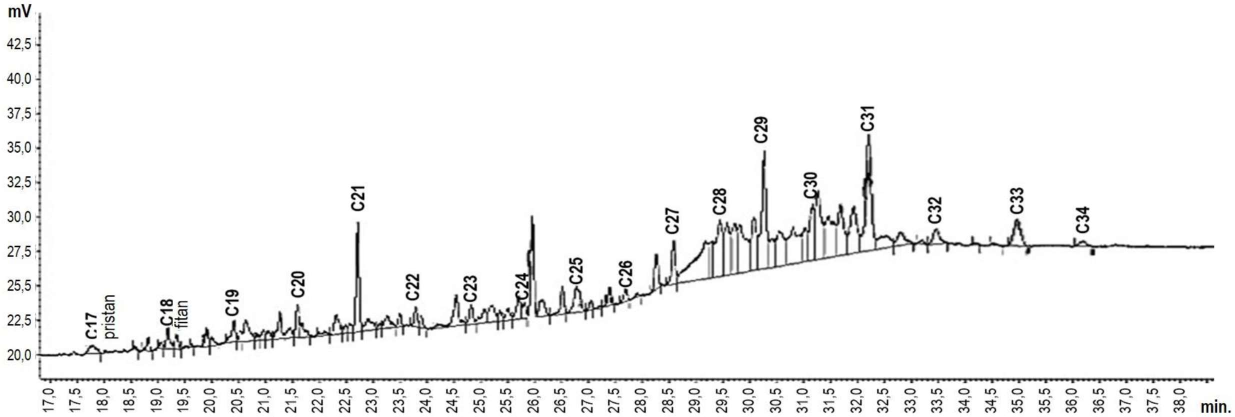

Fig. 5. Typical chromatogram of hydrocarbons with the presence «unresolved complex mixture» of the Long Tau river bottom sediments (st. 2, high tide), 2021

UCM background in bottom sediments was recorded only during high tide. If UCM was evident, it was confined to the high-molecular part of the spectrum (Fig. 5). The ratio of the sum of aliphatic hydrocarbons to the UCM magnitude was 5.05 (Station 1) and 1.42 (Station 2). In the first case we can talk about the presence of an unresolved complex mixture, both due to microbial destruction and the accumulation of man-made organic compounds. At Station 2, located closer to the sea, the portion of the UCM was insignificantly higher, and the value of the ratio in question indicated the presence of fresh oil in the bottom soil of the lower reaches of the Long Tau River during the high tide.

Based on the calculated molecular markers, the terrestrial vegetation can be recognized as the dominant source of hydrocarbon input into the river sediments of the areas studied. This is well explained by the mangroves growing in the Can Gio reserve, through which rivers flow. At the same time, markers that differentiate oil and biogenic hydrocarbons indicate the presence of fresh petrogenic compounds. It should be noted that during high tides, the total aliphatic hydrocarbon concentration increased, an indecomposable background appeared, and the C_{17}/Pr ratio raised; these data, taken together, most likely indicate the input of oil products with river sediments drawn by the tidal flow.

3.2. Content and possible sources of PAHs

The concentration of ∑PAH averaged 354.6±61.7 ng/g at Station 1, at Station 2 it amounted to 267.9±45.7 ng/g (Fig. 6). The content of PAHs in the bottom soil of the Ca Gau River was significantly higher than that of Long Tau River (p_v=0.62). These levels corresponded to nontoxic concentrations [58]. At the same time, at Station 1 the background values were slightly exceeded in the bottom sediments (<300 ng/g). Similar mean concentrations (219 ng/g) were observed in the bottom sediments of the Pearl River Delta (China), which flows along the territory where development of industry, the soil pollution is becoming more and more serious [59]. In Yangtze River, which basin is also the earliest industrialized region in China, the content of PAHs in the bottom sediments was higher (608.5 – 618.6 ng/g depending on the season) [60].

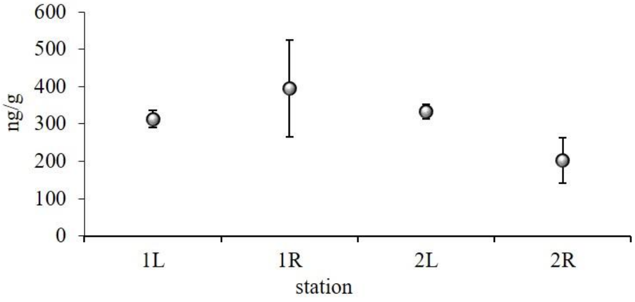

Fig. 6. Average content of ∑PAH (ng/g) in bottom soil of the Ca Gao (st. 1) and Long Tau (st. 2) rivers, 2021.

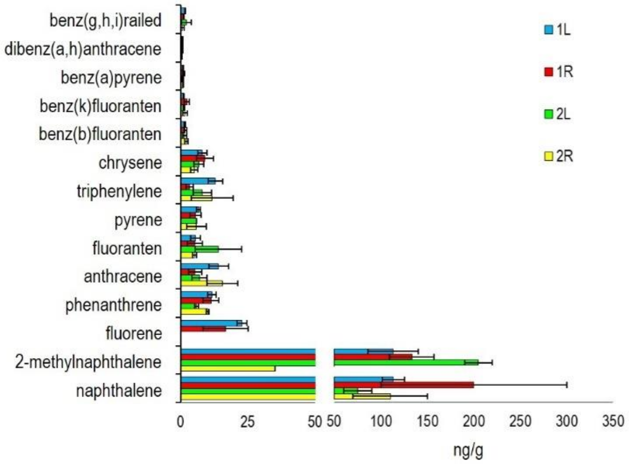

Fig. 7. Composition of PAHs in the bottom sediments of the Ca Gao (st. 1) and Long Tau (st. 2) rivers, 2021.

Taking into account the silty nature of sediments, which contributes to the accumulation of pollutants [61], we can assume the presence of somewhat elevated levels of ∑PAH. According to the method for assessing the level of bottom sediments pollution, with the granulometric composition taken into account [62], the standard content of pollutants is two times higher in silts than in sands.

Twelve PAHs were identified at Station 1 and Station 2 (Fig. 7). It should be mentioned that only trace concentrations of fluorene were found at Station 2.

At both stations, a large portion was accounted for by 2-nuclear naphthalene and methyl-naphthalene, namely, 77% and 80% at Station 1 and Station 2, respectively (Fig. 7).

The total content of polyaromatic compounds was found to increase significantly during high tide at Station 2 located at the mouth of the Long Tau river (Fig. 6), which may indicate their transport by the tidal current from the sea to the river. In the riverbed Ca Gau such a phenomenon was not observed. In the Long Tau river the increase in the total amount of PAHs during high tide occurred mainly due to 2-nuclear compounds (Fig. 8), which, as a rule, were associated with fresh, untransformed oil pollution [63]. Economic activities are constantly increasing in the southern key economic region, especially in Ho Chi Minh City - world's largest river port, which leads to the influx of large amounts of wastewater from this region into Ganh Rai Bay [6]. At the same time, active navigation in this water area can be a one of the sources of pollutants. It is associated with technological and emergency leaks of oil and oil products. The Formosa One incident, for example, occurred in 2001 in Ganh Rai Bay of Ba Ria – Vung Tau province caused a spill of 900 cubic meters of diesel fuel. It is also necessary to take into account the presence of oil production in the Vung Tau area, which can be an additional source of hydrocarbon pollution of the aquatic environment. Thus, the presence of signs of oil pollution is expected for this water area.

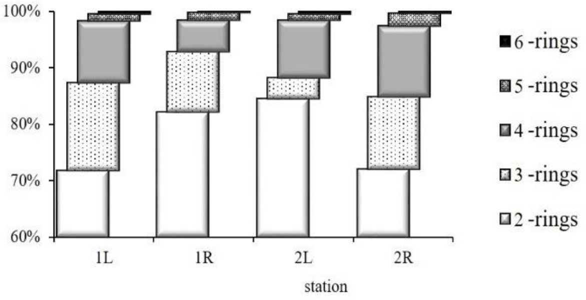

Fig. 8. The ratio of PAHs (%) with the twentieth number of benzene rings in the bottom soil of the Ca Gao (st. 1) and Long Tau (st. 2) rivers, 2021.

In general, the presence of elevated concentrations of the most volatile of polyarenes, naphthalene that is easily destroyed in water, in bottom sediments is atypical. As a rule, it refers to the minor components of PAHs [65]. It should be taken into account that oils contain elevated amounts of methylated compounds [66]. The ratio of naphthalene/2-methylnaphthalene (Table 2) at Station 1 exceeded 1, which indicated that the naphthalene input could not be explained by oil products ingress.

It is possible that the content of naphthalene in bottom soil exceeded the content of its methylated homologue as a result of bacterial degradation of compounds of petrogenic origin, since substituted compounds are destroyed faster than unsubstituted ones [70]. At Station 2 during the high tide, this ratio decreased from 3.14 to 0.37, which indicates the input of a hydrocarbon mixture with signs of fresh oil contamination.

Table 2. Molecular indices for PAHs of pyrolytic and petroleum origin

Index	Mean (with standard error)				Origin		References data
	St. 1L	St. 1R	St. 2L	St. 2R	Pyr.	Pet.	
Naphthalene/2-methylnaphthalene	1.19±0.41	1.35±0.44	0.37±0.10	3.14±1.14	>1	<1	[34]
Phenanthrene/anthracene	0.97±0.29	6.29±4.48	1.05±0.53	0.74±0.25	<10	>15	[67]
Fluoranthene/pyrene	0.81±0.29	0.84±0.19	2.44±1.54	1.36±0.75	>1	<1	[67]
Fluoranthene/ (fluoranthene+pyrene)	0.42±0.09	0.45±0.06	0.64±0.16	0.53±0.15	>0.5	<0.5	[67]
Pyrene/benzo(a)pyrene	8.70±1.44	4.90±0.27	11.91±5.97	6.65±3.06	<1	>1	[68]
(Fluoranthrene+ pyrene)/(phenanthrene+ chrysene)	0.94±0.08	0.84±0.08	0.94±0.15	1.04±0.16	>1	<1	[69]
∑(2-4)/ ∑(5-6)	56.89±5.23	60.13±3.13	84.79±46.03	36.98±4.10	<1	>1	[68]
Benzo(a)pyrene/chrysene	0.11±0.02	0.13±0.03	0.09±0.02	0.17±0.02	>0.35	<0.2	[68]

Notes remarks: Pyr. – pyrolitic origin, Per. – petrogenic origin.

The nature of pollution sources can be identified rather precisely by applying indicator ratios of PAHs. Their use is based on the idea of the preferred formation of one or another isomer in specific processes. Strictly defined isomers are characteristic of specific sources of PAHs, and a change in the ratios over time will indicate, for example, the age of an object or the distance from the source [71]. Most of the calculated indices reveal the presence of oil pollution (Table 2). At the same time, it is possible to judge the insignificant input of PAHs formed as a result of various types of combustion processes.

We observed some quantitative and qualitative changes in the composition of PAHs in the "high-low tide" cycle, therefore we studied the diagnostic indices during high and low tides (Table 2). Though the values of diagnostic indices obtained at Station 1 during periods of high and low tide somewhat differed, their interpretation in both phases was the same. At Station 2, located downstream, where a significant increase in ∑PAH was noted during high tide, there was an increase in the number of indices indicating the petroleum origin of PAHs. The change in the absolute values of the indices also showed a trend towards an increase in the proportion of substances of oil origin. These facts confirm the earlier assumption about the transfer of PAHs in the form of oil components from the East Sea to the lower reaches of the Long Tau River at high tide. The waters and bottom sediments of Ganh Rai Bay being polluted as a result of anthropogenic loading, are likely to be a source of pollution of the relatively cleaner riverbed. A similar phenomenon has been observed in the river-sea water mixing area of the Chernaya River (Black Sea, Sevastopol) [61].

At Station 1, located in the Ca Gau riverbed, the number of indices suggestive of the presence of petrogenic compounds was constant both at high tide and at low tide. It demonstrated the presence of petrogenic compounds in river sediments of the flowing along the reserve. Probably, these PAHs entered the waters of the river in the upper reaches of its course, and further accumulated in the bottom sediments. It was also possible that this class of substances was transported by the sea water brought in during tides.

Benz(a)pyrene is the component whose toxic properties were used to develop the most common method for assessing the toxicity of PAHs.

The toxic equivalent is defined by formula:

$$TEQ=\sum (Ci \times TEFi) \quad [72; 73] \qquad (1)$$

where, TEF – toxic equivalent factor of individual PAHs; Ci – individual PAHs concentration in a mixture.

The total toxicity coefficient of PAHs at Station 1 was 3.1±0.4 ngTEQ/g. At Station 2 it was 2.8±0.5 ngTEQ/g. Such values were low compared to other areas of the World Ocean [74; 75; 76]. A significant share (>10 %) in the formation of bottom sediment toxicity at both stations was due to triphenylene, B(a)P, and dibenz(a,h)anthracene. The total toxicity of binuclear compounds prevailing by weight did not exceed 9 %.

The TEQ index takes into account the toxic carcinogenic effect of a mixture of PAHs. There are also criteria to assess the impact of pollutants, including PAHs, on the bottom community. In particular, the sediment quality guidelines (SQG) indices were developed by the Canadian Council of Ministers of the Environment as broadly protective tools to support the functioning of healthy aquatic ecosystems. It should be noted that the data on this index, calculated only on the basis of the PAHs content in bottom sediments, are limited, since its full calculation also includes a number of other components, such as heavy metals, PCBs, etc.

$$SQG=(\sum C_i/PEL)/n \quad [77; 78] \qquad (2)$$

where, C_i/PEL – the ratio of the concentration of a toxic substance in the sample to the value of PEL (Probable Effect Level); n - the number of toxic components.

To evaluate this index, there are the following criteria: <0.1 – non-toxic bottom sediments; 0.1-1.0 – moderately toxic; >1 – sediments is highly toxic [79]. For the study area, the SQG index of bottom sediments in the analyzed samples ranged from 0.12 to 1.02, averaging to 0.47 at Station 1, and 0.72 – at a more polluted with PAH Station 2. Thus, in accordance to this index, bottom sediments can be considered predominantly medium toxic benthic biota. At the same time, the bottom sediments of the more polluted Ca Gau River were more toxic than Long Tau River.

4. CONCLUSION

1. The content of aliphatic hydrocarbons in river sediments of the Ca Gau River was 41.18±6.94 µg/g, at the outfall of the Long Tau River this figure amounted to 22.60±6.10 µg/g. The content of ∑PAH in the Ca Gau was 354.6±61.7 ng/g, and in the Long Tau mouth it made up 267.9±45.7 ng/g.

2. Based on the calculated molecular markers, the terrestrial vegetation can be considered as the dominant source of AHC input into the river sediments of the areas studied. At the same time, markers that differentiate aliphatic hydrocarbons of oil and biogenic origin indicate the presence of fresh petrogenic compounds. Most of the thermodynamic indices calculated for river sediments of the Ca Gau and Long Tau rivers indicate existence of oil pollution in river sediments of the rivers flowing through the water area of the reserve.

3. At the outfall of the Long Tau River, during tides, most likely happens to the input of oil products along with the river sediments carried by the tidal current.

5. A relatively favorable state of bottom soil of the Ca Gau and Long Tau rivers, flowing through territory of the Can Gio reserve, was recorded in terms of the level of hydrocarbon pollution. The composition of the hydrocarbon mixture indicates the presence of compounds of petroleum origin, which indicates the anthropogenic load on these reservoirs. Judging by the results of the study, the source of man-made load can be both the adjacent marine area and the catchment area of the rivers.

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