

Original article

Organic Matter and Petroleum Hydrocarbons in the Bottom Sediments of Coastal Waters of the Southern Kamchatka Peninsula

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Abstract

Purpose. The purpose of the study is to assess the content and spatial distribution of organic matter and petroleum hydrocarbons in the surface layer of bottom sediments in the coastal waters of the southern Kamchatka Peninsula depending on the sediment grain-size composition and the degree of coastal urbanization.

Methods and Results. The surface (0–3 cm) sediment samples were collected by a box corer aboard the R/V *Professor Multanovskiy* in August–September 2023. The following parameters were determined: grain-size composition – by a combined sieve method, loss on ignition – according to GOST 23740-2016, organic carbon (C_{org}) content – by coulometric analysis, and concentrations of chloroform-extractable substances and petroleum hydrocarbons – by gravimetric and IR spectrometry. The sediments consisted predominantly of silt-sand mixtures, with a higher silt content in the isolated bays. The content of C_{org} ranged from 0.02 to 3.56%, and loss on ignition ranged from 0.86 to 9.87%, with a strong correlation between the indices ($r = 0.91$). The concentrations of petroleum hydrocarbons and chloroform-extractable substances ranged from 0.3 to 93 and 2 to 185 mg/100 g, respectively, with their maxima being observed in Avacha Bay. The minimum concentrations (0.3–3.2 mg/100 g for petroleum hydrocarbons and 2–8 mg/100 g for chloroform-extractable substances) were noted in sandy sediments in the Khalaktyrsky Beach area, as well as in silt sediments of Vilyuchinskaya Bay. The values of both of petroleum hydrocarbons and chloroform-extractable substances positively correlated with C_{org} and loss on ignition. The linear regression model demonstrated that loss on ignition and the urbanization indicator jointly explained about 80% of the variation in $\ln(PhC)$.

Conclusions. The obtained results show that the organic matter content and the grain-size composition of sediments are the key factors controlling the accumulation of petroleum hydrocarbons, while coastal urbanization enhances the hydrocarbon load. Signs of chronic pollution are characteristic of Avacha Bay and several shallow bays.

Keywords: bottom sediments, grain-size composition, organic matter, organic carbon, petroleum hydrocarbons, marine pollution, urbanization, Kamchatka Peninsula, Avacha Bay

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Introduction

Coastal waters of the southern Kamchatka Peninsula are systems influenced by both natural and anthropogenic factors. These zones serve as important buffers between the continent and the sea, accumulating substances supplied by continental runoff, atmospheric precipitation, and human activities [1]. Bottom sediments (BS) act as long-term pollutant sinks, where accumulation, transformation, and partial remobilisation processes occur [2, 3]. The surface sediment layer (0–3 cm) is the most informative for assessing the current state of a water area, because it is where recent pollutant inputs accumulate and active sedimentation processes take place.

Growing coastal urbanisation increases the input of pollutants – heavy metals, petroleum hydrocarbons (PHC), and anthropogenic organic matter – into sediments [4–7]. Geochemical studies reveal that urbanised coasts have significantly higher sediment contamination levels than poorly developed areas [4, 8]. Similar patterns have been found along the Kamchatka coast, where economic activity is particularly pronounced within urban agglomerations and port areas, such as Avacha Bay [9, 10].

Coastal zones are critically important areas of interaction, accounting for 15% of global productivity and over 80% of total organic matter burial [1]. Organic matter plays a key role in shaping the chemical composition and properties of sediments, influencing sorption, complexation, and pollutant retention [11, 12]. It can affect environmental physicochemical conditions, promote reducing conditions, and substantially alter metal and hydrocarbon mobility [2, 11]. It has also been established that the contents of organic carbon and petroleum hydrocarbons correlate positively with the proportion of fine fractions [13–17], confirming the role of these fractions and organic matter in pollutant sorption.

Several studies indicate a direct relationship between coastal urbanisation and the degree of BS contamination [4, 18]. In areas with developed infrastructure, intensive shipping, and wastewater discharge, elevated concentrations of petroleum hydrocarbons, copper, zinc, and lead are observed compared with background levels [9, 19]. Thus, the spatial distribution of organic matter and associated contaminants can be considered an indicator of anthropogenic pressure and the degree of coastal urbanisation [20].

The study aims to investigate the spatial distribution of organic matter and petroleum hydrocarbons in the bottom sediments of coastal waters of the southern Kamchatka Peninsula in relation to sediment grain-size composition, and to identify relationships between their contents and the degree of coastal urbanisation.

Materials and methods

The work was carried out from August 15 to September 20, 2023, during cruise No. 23/4 of the R/V *Professor Multanovskiy* in the south-eastern (Pacific Ocean) and south-western (Sea of Okhotsk) coastal waters of the Kamchatka Peninsula, within the framework of the scientific and educational program “Floating University” (Agreement No. 075-01593-23-06). The location of sediment sampling stations is shown in Fig. 1.

This paper presents the results of the analysis of surface (0–3 cm) sediment samples collected using a box corer. Grain-size composition was determined by a combined sieve method with separation into fractions using a standard set

of sieves (aperture sizes: 10, 7, 5, 2.5, 2, 1, 0.5, 0.25, 0.1, and 0.05 mm, GOST 12536-2014). Fractions larger than 0.05 mm were separated by dry sieving. The pelite-aleurite fraction (≤ 0.05 mm) was separated by wet sieving followed by gravimetric determination of its dry mass.

The total organic matter content of BS was determined by loss on ignition (LOI) (GOST 23740-2016). For the analysis, air-dried samples were ground in a porcelain mortar and sieved with an aperture size of 0.2 mm. The sample mass was 3–5 g. The prepared crucibles containing duplicate sediment samples were dried at $(105 \pm 2)^\circ\text{C}$ to constant mass and then placed in a cold muffle furnace; the temperature was gradually raised to $(525 \pm 25)^\circ\text{C}$, and the samples were ignited for three hours until a constant mass was reached. LOI was calculated from the difference in mass. The final result was taken as the arithmetic mean of two parallel determinations. The difference between the parallel determinations did not exceed 2.5% of the mean value.

Organic carbon (C_{org}) content was determined using an AN-7529M rapid analyser by automatic coulometric titration. The operating principle of the analyser is based on the combustion of a sample aliquot in a purified oxygen stream, the absorption of the resulting carbon dioxide (CO_2) in the electrolytic solution of the cell, and automatic compensation for the pH change in this solution by electrolysis. According to the method adapted for marine sediments [21], a 0.25 g sample aliquot was mixed with 0.25 g of cobalt oxide (Co_3O_4) as a combustion catalyst. The total sample mass did not exceed 0.5 g. The empirically determined combustion time was three minutes. Each sample was analysed in duplicate. A certified reference material (GSO 5359-90 (OOKO152)) was used for quality control. The quality control results were as follows: the standard deviation was 0.03% for samples with a low organic carbon content ($C_{\text{org}} < 0.5\%$) and 0.083% for sediments with an elevated content ($C_{\text{org}} > 1.5\%$).

In the prepared air-dried BS samples, chloroform-extractable substances (CES) were determined gravimetrically, whereas petroleum hydrocarbons were determined by IR spectrometry using an FSM-1201 Fourier-transform infrared spectrometer (InfraSpek CJSC, Russia) following the Oradovskiy method¹. The method is based on the extraction of hydrocarbons with carbon tetrachloride (CCl_4), the purification of the resulting extract on an alumina (Al_2O_3) column to separate non-polar petroleum fractions, and subsequent measurement of the optical density in the infrared region of the spectrum.

Statistical analyses and regression modelling were performed using the R software environment, version 4.3.1 (R Foundation for Statistical Computing, Vienna, Austria). To assess the effects of anthropogenic pressure and sediment properties on PHC concentrations, a linear regression model was applied. The model coefficients were estimated by ordinary least squares.

The dependent variable was the natural logarithm of the PHC concentrations, which reduced the skewness of the data distribution and improved conformity with the assumptions of linear regression:

¹ Oradovskiy, S.G., ed., 1977. *Manual on Methods of Chemical Analysis of Seawater*. Leningrad: Gidrometeoizdat, 208 p. (in Russian).

$$\ln(\text{PHC}) = \beta_0 + \beta_1 \cdot \text{Urban} + \beta_2 \cdot \text{LOI},$$

where *Urban* is a categorical indicator of coastal urbanisation, and LOI is the organic matter content determined by loss on ignition, %.

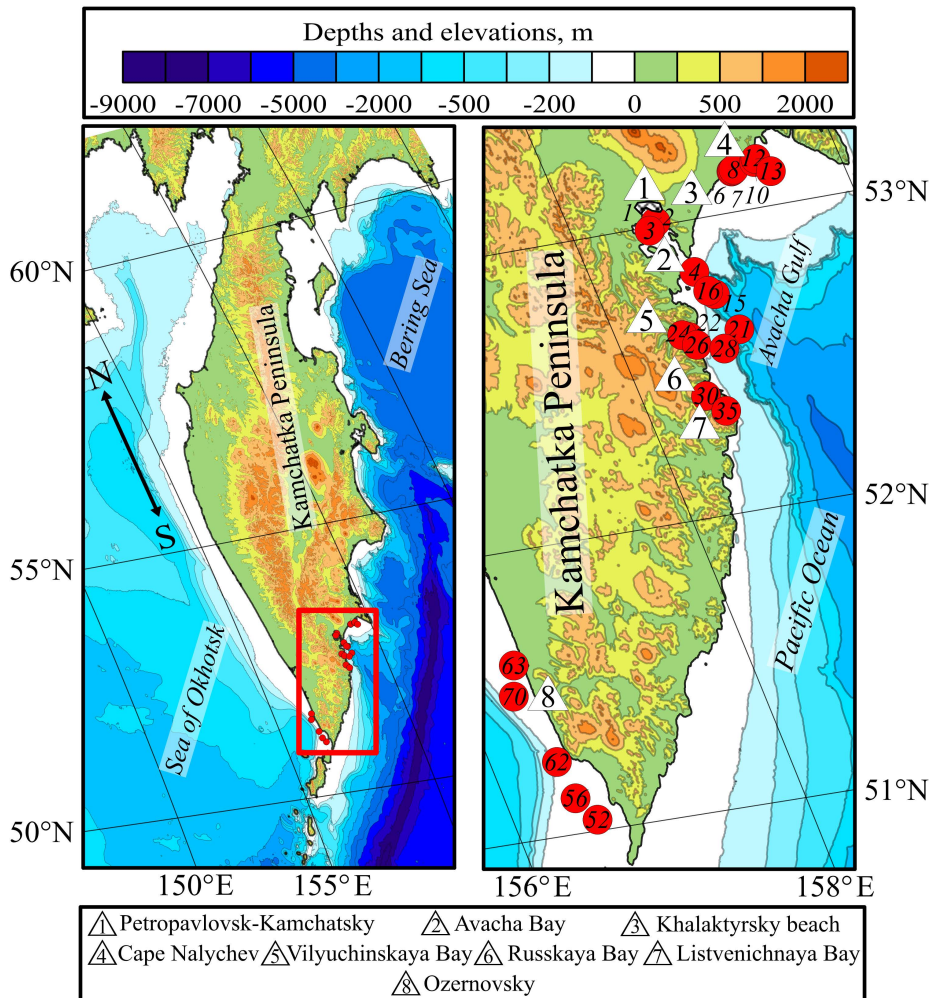


Fig. 1. Study area (shown as a red rectangle in the left fragment) and diagram of the sediment sampling stations (right)

The *Urban* indicator was calculated based on the minimum distance from the sampling station to the nearest coastal settlement or port. The resulting distance gradient was interpreted as a categorical scale of anthropogenic pressure: 0 – background areas (> 60 km), 1 – low-pressure areas (30–60 km), 2 – moderate-pressure areas (10–30 km), and 3 – high-pressure areas (≤ 10 km). We used this classification as an approximate estimate of the spatial gradient of anthropogenic impact associated with the distance of sampling stations from major coastal pollution sources. Approaches based on distance to urbanised territories and infrastructure are used to assess anthropogenic impact on coastal

ecosystems [22, 23]. Distance thresholds were chosen taking into account the scale of the study area and the station distribution relative to settlements and port infrastructure.

When selecting the final model, we also considered C_{org} , grain-size composition, and depth. The models were compared based on the adjusted coefficient of determination, the Akaike information criterion (AIC) [24], the statistical significance of the coefficients, and the presence of multicollinearity among the predictors.

Results and discussion

Analysis of the obtained results revealed that, in terms of grain-size composition, the BS consisted predominantly of silt-sand material (average proportions: silt, 52%; sand, 42%), with minor local inclusions of coarse gravel material (average proportion, 6%) (Fig. 2).

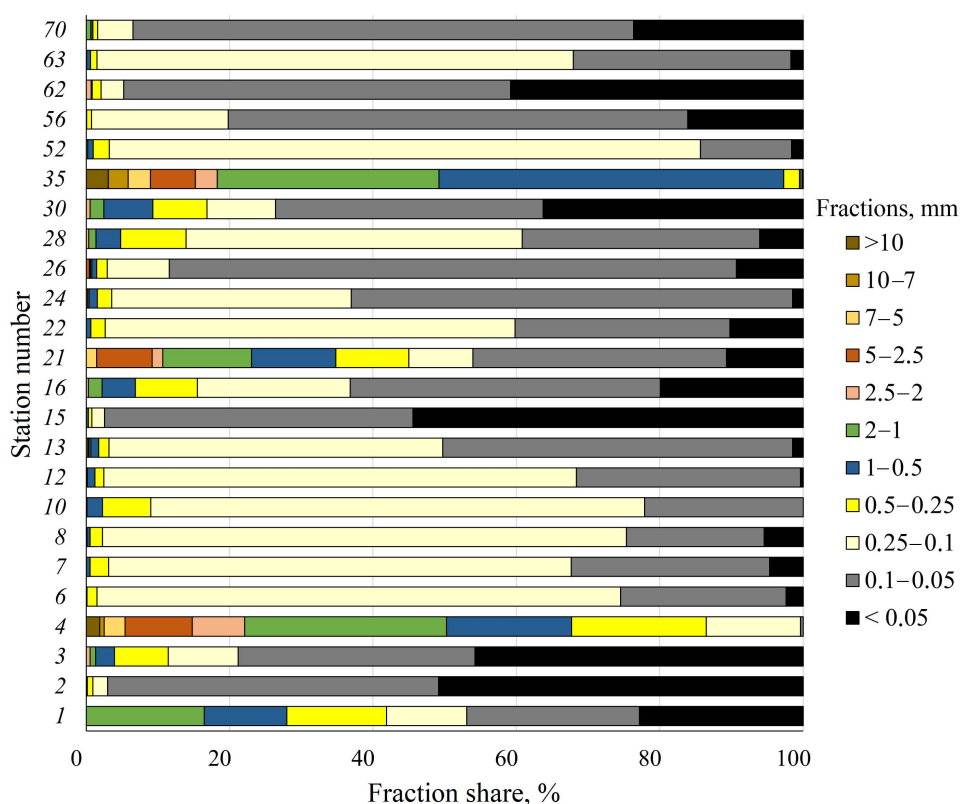


Fig. 2. Diagram of the grain-size composition of the surface layer of bottom sediments in the coastal waters of Kamchatka Peninsula, 2023

As seen in Fig. 3, the organic matter content in the surface layer of BS showed significant spatial variability among stations, indicating heterogeneity in the conditions governing the accumulation and transformation of organic matter in the study area.

C_{org} content in the BS of the studied coastal water areas of the southern Kamchatka Peninsula ranged from 0.02 to 3.56%, reflecting heterogeneity in both substrate lithology and grain-size composition, as well as varying degrees of anthropogenic impact (Fig. 3). Minimum values ($< 0.1\%$) were characteristic of sandy sediments in open areas near Khalaktyrsky Beach (stations 6–8) and Cape Nalychev (stations 10–12), while maximum values ($> 2\%$) were recorded in areas dominated by fine pelitic material: Avacha Bay and Russkaya Bay (stations 1–3, 30). This relationship was confirmed by a strong positive linear correlation ($r = 0.82$, $n = 23$).

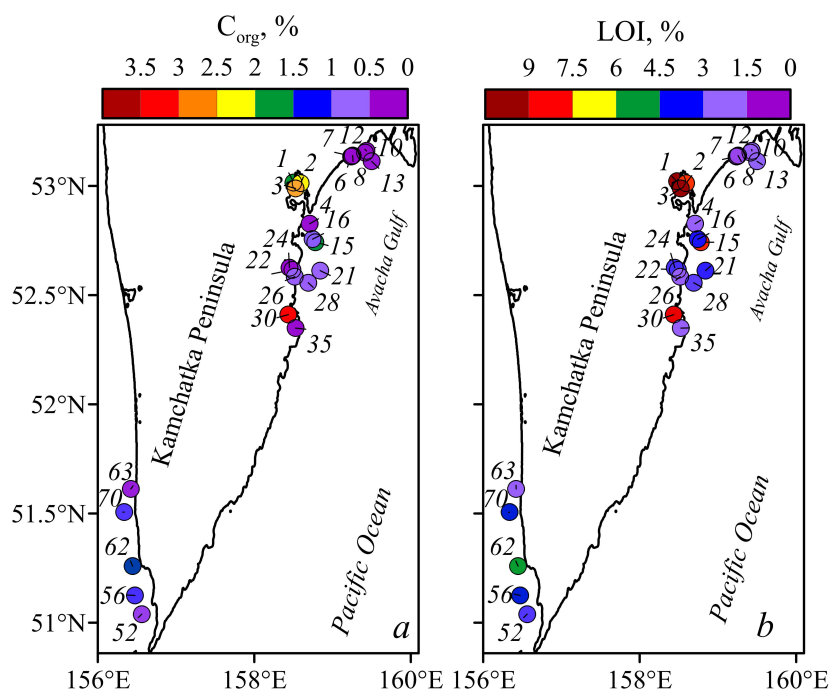


Fig. 3. Content of C_{org} (a) and LOI (b) in the surface layer of bottom sediments in the coastal waters of Kamchatka Peninsula, 2023

LOI values ranged from 0.86 to 9.87% with a strong positive correlation between LOI and C_{org} content ($r = 0.91$, $n = 23$), indicating their partial interchangeability in assessing organic enrichment in sediments. The correlation coefficients between LOI and the grain-size fractions were 0.6 for silt, 0.1 for aleurite, and 0.9 for pelite. For the gravel and sand fractions, the correlation coefficients were negative: -0.1 and -0.6 , respectively.

High C_{org} and LOI values are typical of coastal water areas receiving continuous inputs of allochthonous organic matter from river runoff and wastewater, as well as of areas with limited water exchange where fine material accumulates [17]. Similar patterns were noted in other coastal ecosystems of the Northern Pacific [25, 26].

Concentrations of chloroform-extractable substances ranged from 2 to 185 mg/100 g of air-dried sediment, whereas those of petroleum hydrocarbons ranged from 0.3 to 93 mg/100 g (Fig. 4). Maximum concentrations of both

substances were recorded in BS from Avacha Bay (stations 1–3). These stations were located in areas of high anthropogenic pressure, and the recorded concentrations were consistent with previously published regional environmental monitoring data ².

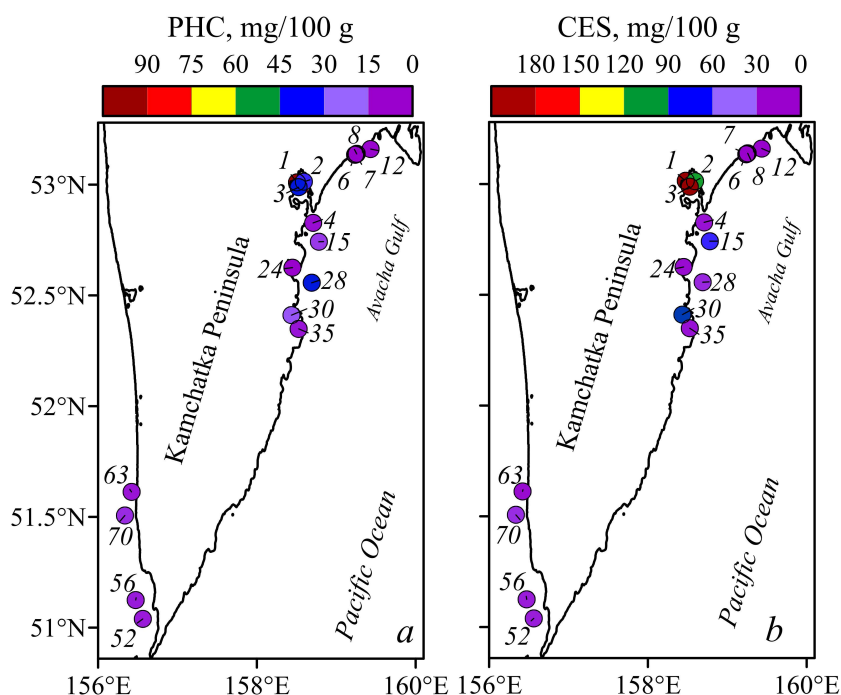


Fig. 4. Content of PHC (a) and CES (b) in the surface layer of bottom sediments in the coastal waters of Kamchatka Peninsula, 2023

Elevated PHC and CES concentrations were also noted at stations 15 and 30, which may be explained by the sediment type (greenish-grey silt with black streaks) and the elevated pelitic material (36–54%) and organic matter (C_{org} , 1.5–3.6%; LOI, 7.3–7.8%). Minimum concentrations (0.3–3.2 mg/100 g for PHC and 2–8 mg/100 g for CES) were observed in sandy sediments in the Khalaktyrsky Beach area, as well as in silt sediments of Vilyuchinskaya Bay (station 24). In the first case, low PHC and CES values may be explained by the sediment type and the low sorption capacity of these sediments; in the second, they may indicate low anthropogenic pressure in this bay, since the sediments there are predominantly fine-grained (silt fraction, 63%) (Fig. 2).

It has been established that petroleum hydrocarbons make the greatest contribution to the pollution of the waters of Avacha Bay [10]. According to the regional classification [27], CES values in sediments at most stations correspond to pollution level I (conventionally clean); those at stations 15, 30, and 2

² Government of Kamchatka Krai, 2023. *Report on the State of the Environment in Kamchatka Krai in 2022*. Petropavlovsk-Kamchatsky: Ministry of Natural Resources and Ecology of Kamchatka Krai, 418 p. [online] Available at: <https://minpri.kamgov.ru/files/64f55ac61dac00.85925865.pdf> [Accessed: 07 July 2026] (in Russian).

correspond to level II (no visible degradation of biocenoses); and those at stations 1 and 3 correspond to level III, indicating the onset of degradation of biocenoses. At station 1, the PHC/CES ratio exceeded 0.5.

A strong positive correlation was found between CES and PHC concentrations ($r = 0.86$, $n = 17$), reflecting their common, predominantly hydrocarbon origin associated with urbanisation, shipping, and port activities. The average PHC/CES ratio was 0.29 (ranging from 0.06 to 0.60). Minimum PHC concentrations were observed at stations 8 and 24, whereas the minimum CES concentration was recorded at station 8, which is located in an area of sand accumulation.

The ability of BS to adsorb PHC depends, among other factors, on their grain-size composition and total organic matter content: as organic matter content and the proportion of the fine pelitic fraction increase, the capacity of sediments to accumulate PHC also increases [28–31]. CES concentrations correlated positively with C_{org} ($r = 0.75$, $n = 17$) and LOI ($r = 0.90$, $n = 15$), indicating the leading role of the organic matrix in the accumulation of non-polar organic compounds.

To assess sediment contamination by PHC, two main approaches are used internationally: comparison with regional regulatory criteria and with background (natural) concentrations. Threshold values indicating contamination vary substantially by region and are > 1.5 mg/100 g for the Persian Gulf [32], > 5 mg/100 g for South African waters ³, and > 50 mg/100 g for Canada ⁴. According to work ⁵, background PHC concentrations in marine silts usually range from 1 to 20 mg/100 g on a dry weight basis, which is consistent with the value of 20 mg/100 g given for the Gulf of Mexico [33, 34].

The parameters and statistical characteristics of the final regression model are given in the Table. The most robust and significant predictor of PHC concentration was organic matter content determined by LOI. To quantitatively assess the contributions of organic matter content and coastal urbanisation, we applied the following regression model:

$$\ln(\text{PHC}) = -0.77 + 0.47 \cdot \text{Urban} + 0.37 \cdot \text{LOI}.$$

Statistical characteristics of the linear regression model

Parameter	Coefficient β	Standard error	t -statistics	p -value
Absent term	-0.766	0.427	-1.793	0.098
<i>Urban</i>	0.472	0.277	1.702	0.114
LOI	0.371	0.079	4.671	0.001

The final regression model explains about 80% of the variation in $\ln(\text{PHC})$ ($R^2 = 0.80$, $Adj R^2 = 0.76$, $AIC = 39.42$, F -statistic = 21.65), with the LOI coefficient

³ DPR, 2002. *Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN)*. Lagos, Nigeria: DPR, 129 p.

⁴ Atlantic PIRI, 2012. *Atlantic RBCA (Risk-Based Corrective Action) for Petroleum Impacted Sites in Atlantic Canada. Version 3. User Guidance*. Canada: Atlantic RBCA, 102 p.

⁵ Kravchenko, E.V. and Bibichkov, A.G., 1988. *Oil Products in Modern Marine Sediments as an Ecological Indicator during Dumping*. Moscow: State Design, Survey and Research Institute of Maritime Transport, 54 p. (in Russian).

being statistically significant ($\beta \approx 0.37$, $n = 15$, $p \approx 0.001$), despite the limited number of observations (Fig. 5). This means that, all other factors being equal (i.e. at the same level of coastal urbanisation), 1% increase in sediment organic matter content determined by LOI is associated with an increase in PHC concentrations by a factor of approximately 1.45, because $\ln(\text{PHC})$ increases by 0.37.

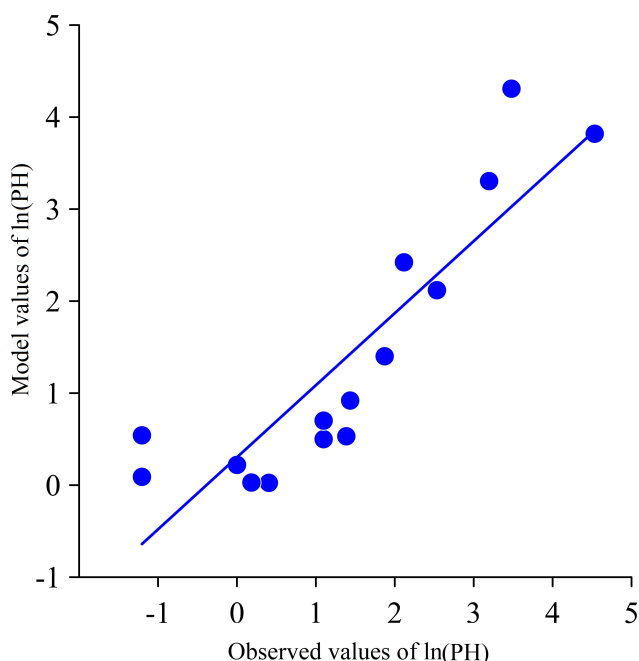


Fig. 5. Relationship between the observed and model-derived values of $\ln(\text{PHC})$ in bottom sediments

When C_{org} was included in the model instead of LOI, the direction of the relationship remained unchanged, but its contribution to explaining the variation in $\ln(\text{PHC})$ was less pronounced. In practice, LOI is a more integrative and sensitive indicator of the sedimentary organic matrix. The pelite-aleurite fraction (< 0.05 mm), although positively correlated with PHC concentration, was not included in the final regression model due to strong multicollinearity with LOI ($r \approx 0.9$), which prevented their effects from being reliably separated given the limited sample size.

The regression results demonstrate a clear tendency for PHC concentrations to increase with proximity to urbanised coastal areas. The coefficient for *Urban* is positive ($\beta \approx 0.47$) and indicates a trend of increasing PHC levels with growing urbanisation (roughly 1.5–1.7-fold increase when moving from one category to another) (Fig. 6). However, given the available number of observations ($n = 15$), its significance is at the level of $p \approx 0.1$.

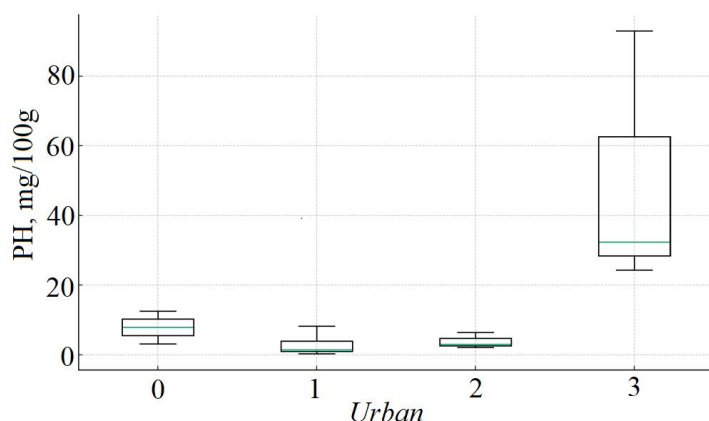


Fig. 6. Distribution of petroleum hydrocarbons along the anthropogenic pressure gradient (*Urban*)

The result emphasises that, even at the same level of anthropogenic pressure, sediments at stations with higher organic matter content accumulate substantially more PHC. Thus, coastal urbanisation influences the baseline level of anthropogenic petroleum hydrocarbon loading, while organic matter content controls the degree of PHC accumulation in sediments. The combined effects of these two factors shape spatial patterns of contamination.

Conclusion

Based on the results of this study, the distribution patterns of organic matter and petroleum hydrocarbons in the bottom sediments of coastal waters of the southern Kamchatka Peninsula were identified. An important factor controlling their spatial differentiation is the sediment grain-size composition. Maximum organic matter contents and petroleum hydrocarbon concentrations were recorded in fine-grained sediments from isolated bays (Avacha Bay and Russkaya Bay).

According to regression analysis, the key factors shaping the spatial distribution of petroleum hydrocarbons in bottom sediments are the level of anthropogenic pressure and organic matter content. The final model explains about 80% of the variation in $\ln(\text{PHC})$ ($R^2 = 0.80$, $Adj R^2 = 0.76$, $AIC = 39.42$, F -statistic = 21.65). All other factors being equal, a 1% increase in LOI corresponds to an approximately 1.45-fold increase in PHC concentration. The coefficient for the anthropogenic pressure indicator indicates a tendency for PHC concentration to increase approximately 1.6-fold when approaching coastal infrastructure zones.

Thus, the spatial distributions of the studied parameters are shaped by the combined influence of lithodynamic conditions, which determine the accumulation of fine organic-rich material, and anthropogenic pressure, which facilitates pollutant input. Isolated bays with high silt content are the most susceptible to petroleum hydrocarbon accumulation, which should be taken into account when assessing risks in urbanised coastal areas of the region.

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