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Baltica

BALTICA Volume 32 Number 1 June 2019: 22–32
https://doi.org/10.5200/baltica.2019.1.3

Oil pollution and geochemical hydrocarbon origin markers in sediments of the Curonian Lagoon and the Nemunas River Delta

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Stakėnienė, R., Jokšas, K., Zinkutė, R., Raudonytė-Svirbutavičienė, E., 2019. Oil pollution and geochemical hydrocarbon origin markers in the Curonian Lagoon and Nemunas River Delta sediments. *Baltica, 32 (1),* 22–32. Vilnius. ISSN 0067–3064.

Manuscript submitted 18 January 2019 / Accepted 29 April 2019 / Published online 20 June 2019

Abstract The continuous research on anthropogenized coastal zones determined qualitative and quantitative characteristics of aliphatic hydrocarbons in the Curonian Lagoon and the Nemunas River Delta. The concentration of aliphatic hydrocarbons varied from 9.1 to 187.6 μg g^{-1} d.w. The Curonian Lagoon could be classified as a slightly contaminated water basin with some moderately polluted areas, while both rivers and Lake Krokų Lanka were found to be slightly contaminated with aliphatic hydrocarbons. The prevailing unresolved complex mixture and geochemical markers suggested the existence of mixed biogenic-anthropogenic aliphatic hydrocarbon sources in the area studied. The biogenic impact was found to be more pronounced in Lake Krokų Lanka, the south-eastern part of the Curonian Lagoon and in the River Minija, while the Nemunas River Avandelta demonstrated the highest loading of anthropogenic hydrocarbons. The same trends were confirmed by the principal component analysis.

Keywords: *transitional water; aliphatic diagnostic ratios; hydrocarbon sources*

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INTRODUCTION

Aliphatic hydrocarbons (ALHs), originating from both natural and anthropogenic sources, occur ubiquitously in various aquatic environments. They could be bio-synthesized by a wide range of marine biota and terrestrial plants or enter the environment via degradation or burning of biological substances (Rostami *et al.* 2019). In addition, aliphatic hydrocarbons are important components of crude oil and its products, which are among the main pollutants in coastal marine ecosystems (Tolosa *et al.* 2004). It has always been crucial to identify the origin of hydrocarbons as well as to estimate their degradation/weathering level. To this end, various qualitative and quantitative ratios might be applied, since many hydrocarbons are source-specific and might be used as geochemical markers for the determination of hydrocarbon origin and oil pollution sources (Commendatore *et al.* 2012; Silva *et al.* 2012; Kanzari *et al.* 2014; Rostami *et al.* 2019).

Regardless of their origin, ALHs undergo a series of changes (dissolution, transfer, sedimentation, weathering, chemical and photo-oxidation) after entering the aqueous environment. Due to their hydrophobic nature, hydrocarbons are eventually associated with particulate material and accumulate in sediments, which are recognized as excellent sinks for pollutants

(Tolosa *et al.* 2004). Sediment thus might reflect the basic trends of organic compounds distribution and the ecological status of the water body (Zaghden *et al.* 2007; Roig *et al.* 2015). Even though ALHs are not included in the priority organic pollutants list, they can easily accumulate in organisms through food chains, presenting a potential threat to aquatic ecosystems and even to human health (Khan *et al.* 2018).

Coastal lagoons experience elevated stress due to their natural parameters (physico-chemical, biological factors) and increasing anthropogenic activity (coastal pollution, oil spills, fishing activity and tourism, eutrophication, etc. (Ünlü, Alpar 2017). The Curonian Lagoon is one of the largest estuarine coastal freshwater lagoons in the Baltic Sea region, experiencing anthropogenic threats from the Nemunas River basin and the Klaipėda Port (Emelyanov *et al.* 2015). Even though pollution of the Curonian Lagoon was extensively studied in the past (Jokšas *et al.* 1998; Pustelnikovas 1998; Jokšas *et al.* 2003; Emelyanov *et al.* 2015; Suzdalev 2015; Jokšas *et al.* 2016), comprehensive data on its recent organic pollution are lacking. It was only in the northern part of the Lagoon (Klaipėda Port area) that aliphatic hydrocarbons were more extensively analysed in 2014–2016 (Suzdalev, Gulbinskas 2014; Stakėnienė *et al.* 2016), however, these studies covered neither the central part of the Lagoon, nor the Nemunas River Delta. The Nemunas River being the main source of water and sedimentary material in the Lagoon (Emelyanov *et al.* 2015), anthropogenic pollution sources within its basin are likely to significantly contribute to the environmental status of the Curonian Lagoon. Hence, more attention should be given to both the Nemunas River Delta and Avandelta. The aim of this work was to continue research on anthropogenized coastal zones and (1) to determine qualitative and quantitative characteristics of aliphatic hydrocarbons in the Curonian Lagoon and the Nemunas River Delta; (2) to reveal potential natural and anthropogenic sources and their contribution to different parts of the area studied.

MATERIALS AND METHODS

Study area

The area of this study covers the Lithuanian part of the Curonian Lagoon and the Nemunas River Delta together with adjacent eutrophic Lake Krokų Lanka (Fig. 1).

The Curonian Lagoon collects water from the area of more than 100 thous. sq. km, its main water inflow (98%) coming from the Nemunas River basin. Approx. 22 km^3 of fresh water passes the Lagoon annually as river runoff (Jakimavičius *et al.* 2018). The central part of the Lagoon experiences direct impact of the Nemunas River and is exposed to contamination from anthropogenic sources within the River basin. The latter area is characterised by heterogeneous bottom geomorphology and varying sediment type (Pustelnikovas 1998). Meanwhile, the northern part of the Lagoon is a transitory zone: the narrow Klaipėda Strait connects the Lagoon and the Baltic Sea. Moreover, the Klaipėda Port, facing high risk of contamination, is situated in this part of the Lagoon (Jokšas *et al.* 2003; Stakėnienė *et al.* 2016).

The eastern coast of the Lagoon is mostly low, boggy and peaty. Vast and shallow (depth of 2–3 m) Lake Krokų Lanka is situated in the mouth of the Atmata River, which is the largest deep-water arm of the Nemunas River Delta (Fig. 1). The aforementioned lake serves as a trap for the river sedimentary material. Limited water exchange and silty bottom sediment create perfect conditions for the accumulation of various pollutants (Pustelnikovas 1998).

Sediment sampling

In the summer of 2013–2014, surface (0–3 cm) bottom sediment samples were collected from the Lithuanian part of the Curonian Lagoon up to the Baltic Sea foreshore (at the gateway to Klaipėda Port).

Locations of sampling sites were chosen so that samples from different sedimentation zones and of various contamination levels would be provided (Jokšas *et al.* 2016; Remeikaitė-Nikienė *et al.* 2016). Twenty three samples (L1–L23) were collected from the Curonian Lagoon, including six samples from the Klaipėda port area (L1–L6) and three from the Kniaupas Bay (L21–L23). Seven samples were collected from the Nemunas River arms and channels (R1–R7), while four more sampling stations were situated in Lake Krokų Lanka (K1–K4) (Fig. 1 and Table 1). Sampling was performed with a Van-Veen grab sampler. All the collected samples were wrapped in precleaned aluminium foil, kept in a cooler during the transportation and stored at –20°C in a refrigerator prior to the analysis.

Sample preparation and hydrocarbon analysis

Sediment samples were freeze-dried, passed through <2 mm sieves and milled to powder with a Retsch Mixer Mill MM 400 with zirconium oxide grinding jars and grinding balls. An aliquot of each sample was analysed for total organic carbon (TOC). The below summarised analytical procedure for hydrocarbons is based on ISO 16703:2004. A 20–30 g aliquot of dried and homogenised sediment sample was spiked with RTW-standard solution of n-decane and n-tetracontane and extracted by mechanical shaking (200 rpm) with n-hexane (Sigma-Aldrich, HPLC

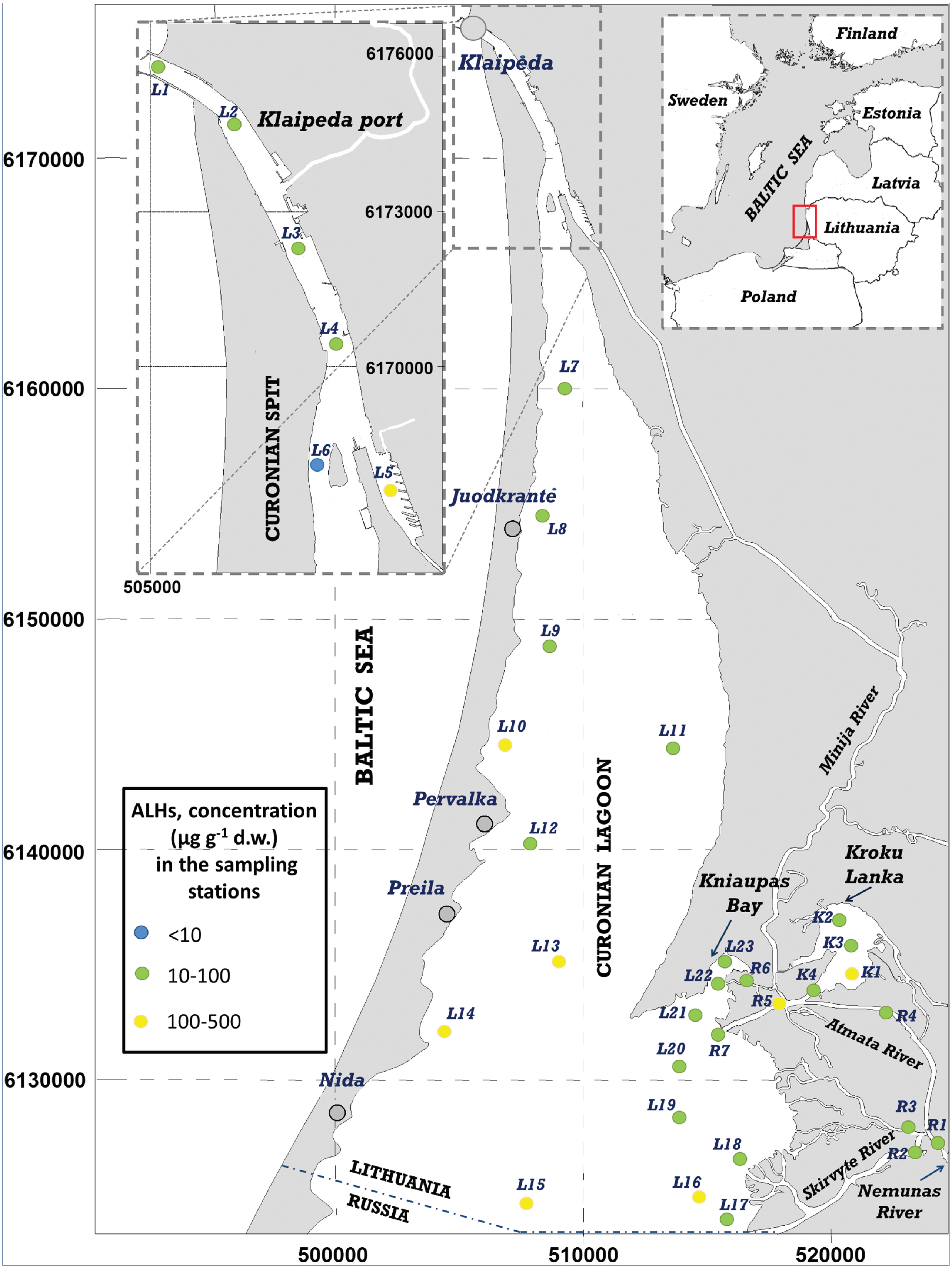

Fig. 1 Study area and sampling stations: Curonian Lagoon, L1–L23; the Lake Krokų Lanka, K1–K4; Nemunas River arms and channels R1–R7. Colours represent contamination level of each sampling station

Table 1 TOC, fine fraction (<0.063 mm) content (Fr), aliphatic hydrocarbons (ALHs) concentrations (d. w.) and geochemical ALHs markers in the bottom sediments from Curonian Lagoon and Nemunas River Delta

	Station	Fr, %	TOC, %	ALHs, µg g^{-1}	UCM, µg g^{-1}	R, µg g^{-1}	UCM/R	R/TOC $*10^{-4}$	Pr/Ph	LMW/HMW	CPI	TAR	NAR
Curonian Lagoon	**L1**	6.2	0.7	19.1	16.5	2.6	6.4	3.8	0.61	3.82	1.56	0.21	0.20
	L2	11.2	2.5	43.9	41.3	2.6	15.8	1.0	1.09	0.78	2.34	1.25	0.32
	L3	12.8	0.7	18.8	16.0	2.7	5.8	3.9	0.90	2.20	1.50	0.39	0.16
	L4	29.4	1.3	23.6	20.1	3.6	5.6	2.7	0.70	3.68	1.56	0.26	0.37
	L5	48.6	4.6	187.6	177.5	10.1	17.6	2.2	1.35	0.80	2.80	1.06	0.40
	L6	2.6	0.4	9.1	8.3	0.7	11.5	2.0	1.14	2.61	1.12	0.25	0.17
	L7	4.0	0.1	20.1	17.7	2.5	7.1	17.2	0.44	6.20	0.73	0.24	–0.02
	L8	7.7	0.4	71.3	67.2	4.1	16.3	10.3	0.50	5.27	0.71	0.37	0.05
	L9	8.9	0.7	84.1	78.9	5.2	15.3	7.6	0.50	4.90	0.72	0.40	0.05
	L10	45.4	4.6	148.0	133.8	14.2	9.4	3.1	0.81	0.68	1.79	2.49	0.41
	L11	0.9	0.4	16.0	14.7	1.3	11.7	3.6	0.51	4.25	0.86	0.35	0.09
	L12	4.1	0.2	66.8	64.0	2.8	22.8	12.2	0.52	3.13	1.03	0.37	0.05
	L13	50.4	2.9	117.2	109.6	7.7	14.3	2.7	1.00	0.61	1.23	1.89	0.17
	L14	55.6	5.4	130.6	118.2	12.4	9.6	2.3	0.88	0.65	1.52	2.18	0.31
	L15	30.8	2.8	114.4	103.4	11.0	9.4	3.9	0.86	0.65	1.47	2.21	0.29
	L16	49.7	3.0	103.5	96.4	7.1	13.6	2.4	0.79	0.66	1.36	2.41	0.25
	L17	0.7	0.1	137.5	133.1	4.4	29.9	44.5	0.40	1.02	0.74	1.56	–0.06
	L18	0.8	0.2	79.9	75.5	4.4	17.2	21.9	0.73	0.43	0.92	3.41	–0.05
	L19	9.9	1.1	57.3	54.8	2.5	22.0	2.3	0.53	0.36	1.26	3.12	0.11
	L20	1.0	0.6	44.4	38.1	6.3	6.0	10.0	0.55	1.21	0.74	0.73	–0.10
	L21	19.3	0.6	10.2	8.6	1.6	5.5	2.8	1.01	0.94	2.32	2.59	0.61
	L22	52.7	3.2	30.7	25.8	5.0	5.2	1.6	0.84	0.32	3.80	4.81	0.66
	L23	59.4	5.7	50.8	36.5	14.3	2.6	2.5	1.25	0.21	3.06	6.98	0.54
	Average	22.3 ± 21.6	1.8 ± 1.8	68.9 ± 51.0	63.3 ± 48.3	5.6 ± 4.	12.2 ± 6.8	7.2 ± 9.7	0.78 ± 0.27	1.97 ± 1.85	1.53 ± 0.8	1.72 ± 1.7	0.22 ± 0.21
Krokų Lanka	**K1**	53.9	5.1	101.8	91.7	10.1	9.1	2.0	1.21	0.38	3.69	3.18	0.63
	K2	51.2	4.3	80.7	72.4	8.2	8.8	1.9	1.23	0.38	2.64	2.59	0.48
	K3	49.7	3.6	57.2	50.3	6.9	7.3	1.9	1.07	0.47	3.49	2.39	0.66
	K4	50.4	3.8	96.7	85.2	11.5	7.2	3.1	1.42	0.29	3.66	4.42	0.63
	Average	51.3 ± 1.8	4.2 ± 0.6	84.1 ± 20.1	74.9 ± 18.3	9.2 ± 2.0	8.1 ± 1.0	2.2 ± 0.5	1.23 ± 0.15	0.38 ± 0.07	3.37 ± 0.5	3.14 ± 0.9	0.60 ± 0.08
Nemunas River arms/channels	**R1**	0.5	0.1	36.8	36.2	0.6	60.8	6.0	0.35	16.27	1.19	0.13	0.21
	R2	0.8	0.1	29.4	28.6	0.8	34.6	16.5	0.37	n.d	0.82	n.d	–0.07
	R3	7.5	0.1	35.1	34.6	0.5	64.6	5.4	0.41	6.51	1.61	0.22	0.38
	R4	3.3	0.5	38.5	38.0	0.4	86.3	0.9	0.22	n.d	1.22	n.d	0.34
	R5	0.6	0.8	100.1	96.8	3.3	29.2	4.1	0.42	1.27	2.27	1.71	0.69
	R6	6.9	0.4	48.8	47.9	0.8	57.0	2.3	0.75	n.d	1.37	n.d	0.54
	R7	5.7	0.1	45.2	44.4	0.9	51.8	6.6	0.32	n.d	0.81	n.d	0.18
	Average	3.6 ± 3.1	0.3 ± 0.3	47.7 ± 24.	46.6 ± 23	1.1 ± 1.0	54.9 ± 19.2	6.0 ± 5.1	0.41 ± 0.17	8.02 ± 7.61	1.33 ± 0.5	0.69 ± 0.89	0.33 ± 0.25

Pr – pristane, Ph – phytane;

R – resolved aliphatic hydrocarbons = n-alkanes$\sum C_{11\text{-}36}$+Pr+Ph;

UCM – unresolved complex mixture = ALHs-R; LMH/HMW = $\sum C_{14\text{-}22}/\sum C_{23}–C_{31}$;

CPI (odd/even) = odd n-alkanes$\sum C_{15\text{-}31}$/even n-alkanes $\sum C_{14\text{-}30}$;

TAR = n-alkanes $(C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19})$;

NAR = (n-alk $\sum C_{19\text{-}32}$–2×even n-alkanes $\sum C_{20\text{-}32}$)/n-alk $\sum C_{19\text{-}32}$

grade) for 12 h. Subsequently, samples were centrifuged at 2000 rpm for 30 min. Extracts were concentrated to a volume of 2 mL using a rotary evaporator and cleaned using Florisil cartridges (Chromabond 6 ml/500 mg). Subsequently, they were eluted with 20 ml of hexane, the as-prepared sample was preconcentrated in a rotary evaporator down to a volume of 0.5 mL. Blank samples were prepared following the same analytical procedure.

ALHs were analysed using a gas chromatograph GC-2010 Plus (Shimadzu) with a flame ionisation detector operating in the splitless injection mode. A fused silica capillary column Rxi1-ms (30 m × 0.25 mm i.d. × 0.25 µm) was applied for the separation of organic compounds. The temperature program used consisted of 60°C for 5 min, 60–315°C at 10° C/min and 315°C for 20 min. Helium was used as a carrier gas at a flow rate of 1.86 mL/min. Linear velocity

(40 cm/s) was set as a flow control mode. The reference standard of diesel/mineral oil in hexane (Restek) was used to determine the total aliphatic hydrocarbon (ALHs) content and to identify the unresolved complex mixture (UCM), while the standard mixture of n-alkanes (C_{10-40}) in hexane (Restek) was applied for the identification and quantification of each hydrocarbon.

Replicate samples (n = 3) and procedural blanks were used for quality control. Relative standard deviation (RSD) was less than 10%, signals of analytes were lower than the estimated limit of detection (LOD) in blank samples. C_{10} and C_{40} were used as internal standards for n-alkane analysis. The recoveries of all n-alkanes were in the range of 65–110%. Limits of detection (LOD) and limits of quantification (LOQ) were estimated as the average signal of the blanks plus three times the standard deviation of the signal of the blanks and average signal of the blanks plus ten times the standard deviation of the signal of the blanks, respectively. LOD varied from 0.08 to 0.2 for individual n-alkanes, whereas LOQ was between 0.15 and 0.4.

TOC and grain size analysis

After removal of inorganic carbon by hydrochloric acid, total organic carbon (TOC) was determined by a high-temperature oxidation method using an elemental analyser liquiTOC (Elementar analysensysteme GmbH, Hanau, Germany). The procedure involves heating the sample at 950°C and measuring the combustion products by an infrared energy detector with a precision of ± 1% (Leong, Tanner 1999). For quality-control samples (n = 14), the mean recovery was 98.7%, the coefficient of variation was 0.34% and below 10% for double analysis of the samples.

The grain size of bottom sediment samples was determined by the classical sieve method (Folk 1974) to establish the percentage of silt (<0.063 mm), sand (0.63–2 mm) and coarser fraction (>2 mm). The latter fraction was not included in our study and calculations. Based on the fine fraction content, sediment was described as sandy (fine fraction content below 50%) and silty (fine fraction content above 50%).

Statistical analysis

Statistical analysis was performed using the Statistica 8.0 software. Pearson's correlation coefficients were applied for the determination of relationships between various parameters. Statistical methods were employed in order to determine distribution peculiarities of aliphatic hydrocarbons in the study area. Relationships between the hydrocarbon concentration and the sediment grain size, and also between the hydrocarbon concentration and the organic matter content were analysed. The principal component analysis with Varimax rotation (to obtain a simpler structure and better interpretation of factor loadings) as well as computation of factor scores of n-alkane concentrations were performed in order to identify the possible sources of ALHs.

RESULTS AND DISCUSSION

Hydrocarbon loading and distribution

The concentration of ALHs in bottom sediments of the study area varied from 9.1 to 187.6 μg g^{-1} d.w., higher concentrations being, as a rule, observed in the fine sediment fraction rich in organic carbon (Table 1). Likewise, more individual n-alkanes were detected in sediments containing a relatively high amount of TOC. A significant positive correlation was observed between ALHs and TOC (Pearson's correlation coefficient 0.56; $p < 0.001$), as well as between ALHs and fine fraction (Pearson's correlation coefficient 0.48; $p < 0.001$).

Sediment is considered to be unpolluted if it contains not more than 10 μg g^{-1} d.w. ALHs (Esteves *et al.* 2006; Zaghden *et al.* 2007; Commendatore *et al.* 2012). When ALHs values are between 10 and 50 μg g^{-1} d.w., a more precise hydrocarbon composition analysis is required, while the concentrations exceeding 100 μg g^{-1} d.w. suggest the presence of petroleum and its products (Readman *et al.* 2002). Sediment can be also assessed according to its contamination level (Commendatore *et al.* 2012): non-polluted (<10 μg g^{-1} d.w.), low-polluted (10–100 μg g^{-1} d.w.), moderately polluted (100–500 μg g^{-1} d.w.) and highly polluted (>500 μg g^{-1} d.w.).

ALHs concentration exceeded 10 μg g^{-1} d.w. at all sampling stations in the Curonian Lagoon, except for L6. Higher than 100 μg g^{-1} d.w. ALHs values were recorded in places with favourable conditions for pollutant accumulation: semi-enclosed bays (L5, L10; Fig. 1, Table 1) and deeper-bottom sites (L14, L15, L16; Fig. 1, Table 1). The mean ALHs concentration was 46.8 ± 36.2 μg g^{-1} d.w. for sandy sediments, while almost twice higher value (110.4 ± 50.4 μg g^{-1} d.w.) was detected in silty sediments.

The anthropogenic input from the Klaipėda Harbour together with specific sedimentary conditions is to blame for the elevated ALHs level in the northern part of the Curonian Lagoon: station L5 exhibited the maximum ALHs concentration of 187.6 μg g^{-1} d.w. (Table 1). Hydrodynamic processes have a huge influence on the distribution of hydrocarbons in sediments. Both organic carbon and pollutants tend to accumulate in areas of limited water circulation, while high organic matter content in sediment facilitates pollutants sorption onto sediment (Jokšas *et al.* 2003; Legorburu *et al.* 2014). ALHs concentration might reach 1500–1600 μg g^{-1} d.w. in the semi-enclosed aquatories with an intense anthropogenic input (e.g. long-term ship anchorage locations and ship-repair dockyards) (Suzdalev, Gulbinskas 2014; Stakėnienė *et al.* 2016).

High ALHs concentrations (137.5 μg g^{-1} d.w. for L17 and 79.9 μg g^{-1} d.w. for L18) were detected in sandy sediment from the Nemunas River Avandelta region. Such a trend, uncommon for coarse sediment, could be closely related to the intense geochemical processes occurring in the river-lagoon barrier zone (Emelyanov 2011).

Sand was the dominant sediment type in the rivers, the mean ALHs concentration (47.7±24.0 μg g^{-1} d.w.) was similar to that detected in sandy sediments of the Lagoon. The highest value reaching 100.1 μg g^{-1} d.w. was recorded in the Nemunas tributary Minija (R5).

The relatively enclosed and shallow Lake Krokų Lanka exhibited the highest mean ALHs value (84.1 ± 20.1 μg g^{-1} d.w.), which could be explained by the high content of fine fraction and TOC, as well as by a slowdown in hydrodynamic processes.

It should be added that no samples were collected from the Klaipėda Strait areas, which were previously discovered to be highly contaminated (Suzdalev, Gulbinskas 2014; Stakėnienė *et al.* 2016). Such sites are located in the northern part of the Curonian Lagoon, the Klaipėda Port area. Anthropogenic input and prevalence of silty sediment are undoubtedly responsible for the elevated pollution levels in this part of the Lagoon.

Based on the detected ALHs values, it could be concluded that both Lake Krokų Lanka and the rivers attributable to the Nemunas River Delta region are slightly contaminated. The Curonian Lagoon could be classified as a slightly contaminated aquatory with some moderately polluted areas in the Nemunas River Avandelta, semi-enclosed bays and deeper sites. In general, ALHs levels in the aquatories studied are much lower than those in polluted/highly polluted areas, such as the Vistula Lagoon Port (630 μg g^{-1} d.w.) (Staniszewska *et al.* 2013) or the Sfax/Gabès Gulf (16–1729 μg g^{-1} d.w.) (Zaghden *et al.* 2007) and are rather comparable to the concentrations detected in low- or moderately contaminated sites, such as Slovenia's coastline (14.0–78.1 μg g^{-1} d.w.) (Bajt 2012) or the Marseille Bay (7–187 μg g^{-1} d.w.) (Asia *et al.* 2009). In comparison to the ALHs concentrations (0.4–152 μg g^{-1} d.w.) and the background values (<10 μg g^{-1} d.w. in sand and <50 μg g^{-1} d.w. in silt) determined in the Curonian Lagoon (excluding the Klaipėda port) more than a decade ago (Jokšas *et al.* 2003; Jokšas *et al.* 2005), ALHs loading in coarse sediment has increased. This could be explained by both increased anthropogenic pressure and more intense bioproductivity. Despite a significant reduction in external nutrient loads over the 1990–2010 period, the local climate change in the Baltic region is a probable reason for the ongoing eutrophication and harmful algal blooms in the Curonian Lagoon (Aleksandrov *et al.* 2018).

Hydrocarbon composition, geochemical markers and sources

Although the composition of aliphatic hydrocarbons and their geochemical markers in each sedimentary environment vary (Table 1), some trends could be observed. In most of the samples, unresolved complex mixture constituted around 80%, which might indicate either the fresh input of petroleum or the presence of degraded/weathered hydrocarbons and oil residues (Farrington, Tripp 1977; Rostami *et al.* 2019). It should be highlighted that the unimodal structure ("hump") with a maximum in the $C_{16–25}$ range was characteristic of UCM in each sedimentary environment. This could suggest the presence of weathered fuel oil (Tolosa *et al.* 2004). However, some authors noted that UCM distributions, mainly in the lower molecular weight range, could be also attributed to the bacterial degradation of natural organic matter (Venkatesan, Kaplan 1982; Tolosa *et al.* 2004).

Distribution of individual n-alkanes exhibited two maximums: for the short chain n-alkanes in the $C_{14\text{-}18}$ range, for the long chain alkanes in the $C_{27\text{-}29}$ range. This could be related to at least two possible sources. Usually, the dominance of odd n-alkanes is attributed to natural sources, while the prevalence of even n-alkanes indicates the anthropogenic origin (Sanil Kumar *et al.* 2016).

In order to assess the origin of hydrocarbons, a set of indicators was applied. The so-called geochemical markers were obtained from separate studies on aliphatic hydrocarbons, each of them revealing the character of pollution at a specific interval.

The ratio of unresolved to resolved aliphatic hydrocarbons compounds (UCM/R) is an estimator of the relative oil degradation degree in sediment. Values higher than 4 indicate the developing biodegradation process and the elevated sediment pollution (Tolosa *et al.* 2004; Rostami *et al.* 2019). High UCM with low concentrations of resolved aliphatic hydrocarbons might represent long-term oil pollution in the region (Commendatore *et al.* 2012). Continuous petroleum hydrocarbon loading with a varying degradation ratio has been already revealed in the study area. The lowest UCM/R values (8.1 ± 1.0) indicating the relatively light anthropogenic pressure were obtained for the sediments from Krokų Lanka Lake, slightly higher ones were recorded in the Lagoon (12.2 ± 6.8), while the rivers exhibited the maximum UCM/R values (54.9 ± 19.2). In each sedimentary zone, UCM/R values were well above 4, which shows that relatively high ALHs loading together with advanced degradation is characteristic of each sedimentary zone (Rostami *et al.* 2019).

The ratio of isoprenoids pristane (Pr) and phytane (Ph) Pr/Ph is indicative of petroleum contamination (Volkman *et al.* 1987). Pr/Ph values ranging between 3 and 5 characterise unpolluted sediment, while those around 1 or lower reveal petroleum pollution (Steinhauer, Boehm 1992). Only a few of all the Curonian Lagoon samples studied demonstrated values slightly higher than 1 (L2, L5, L6, L21, L23; Fig. 1; Table 1), while all samples from Krokų Lanka Lake (K1–K4; Fig. 1; Table 1) exhibited values above 1. Low *Pr/Ph* values were recorded in the rest of samples.

Natural n-alkane ratio (NAR), which is used to estimate the ratio of 'natural' to anthropogenic petroleum alkanes, averaged 0.22 ± 0.21 in the Curonian Lagoon and 0.33 ± 0.25 in the rivers. NAR values closer to 0 suggest the prevalence of anthropogenic hydrocarbons over natural ones (Mille *et al.* 2007; Commendatore *et al.* 2012). Only in the south-western part of the Curonian Lagoon (L21–L23; Fig. 1, Table 1), in the River Minija (R5; Fig. 1, Table 1) and Lake Krokų Lanka (K1–K4; Fig. 1, Table 1), NAR values were closer to 1. The highest input of biogenic hydrocarbons was recorded in sediment from Krokų Lanka Lake (NAR averaged around 0.60 ± 0.08).

The ratio of low to high molecular weight hydrocarbons (LMW/HMW) lower than 1 usually represents terrestrial n-alkanes produced by higher plants, marine animals and sedimentary bacteria (Wang *et al.* 2006). Such values were detected in Lake Krokų Lanka, as well as in some specific sites of the Curonian Lagoon (Table 1), usually in those containing fine sediment. On the contrary, much higher LMW/HMW values were observed for the rivers and sandy sediments from the Curonian Lagoon. Such predominance of LMW n-alkanes in sediments can be due to the inputs of both petroleum and plankton sources (Wang *et al.* 2006).

Carbon preference index (CPI) is defined as the ratio of the sum of concentrations of alkanes with an odd carbon number versus the sum of alkanes with an even carbon number (Yang *et al.* 2018). CPI value is about 1 for crude oil and petroleum hydrocarbons, while values above 1 are indicative of the biogenic input (Farrington, Tripp, 1977).

CPI values were found to be close to 1 in both rivers (1.33 ± 0.50) and the Curonian Lagoon (1.53 ± 0.83). This could be related to crude oil and petroleum hydrocarbons (Volkman *et al.* 2008) originating from vehicular emission and other anthropogenic activities (Mandalakis *et al.* 2002; Wang, Fingas 2003). While odd n-alkanes prevailed amongst LMW alkanes in the northern part of the Curonian Lagoon (L1–L6), Kniaupas Bay (L22–L23) and Lake Krokų Lanka, the dominance of even n-alkanes in the LMW range was observed in the rest of the area studied. High concentrations of even LMW n-alkanes are usually attributed to the fresh input of light oil (Tolosa *et al.* 2004). Even though rather uncommon, the prevalence of even C_{14-22} n-alkanes is sometimes observed in sediments from coastlines, lakes or estuarine-lagoon systems and is believed to be related to the presence of bacteria, algae or fungi (Grimalt, Albaigés 1987; Silva *et al.* 2012). The potential impact of biogenic allochtonic organic carbon should not be negligible in our case either. Sources of low molecular weight n-alkanes might be related to autochtonic bacteria (Jiménez *et al.* 2011) or to those coming from the sea (Nishimura, Baker 1986). Moreover, the mix of different bacteria might also enter the transitional river-lagoon-sea system from the soil (Silva *et al.* 2012). As the Curonian Lagoon is a heavily eutrophicated water body containing high amounts of phyto- and bacterioplankton (Sulcius *et al.* 2015), there is a high possibility that some n-alkanes originate from bacterial activity. The distribution of biogenic LMW n-alkanes might have been affected by such factors as depth, water salinity and nutrients amount (Šulčius *et al.* 2018).

Relatively high CPI values (3.37 ± 0.5) and prevalence of higher molecular mass odd n-alkanes (C_{27-31}) were characteristic of the lake studied. Both factors are related to the biogenic input (Meyers, Ishiwatari, 1993; Volkman *et al.* 2008; Syakty *et al.* 2013). Moreover, amongst LMW compounds, odd n-alkanes (C_{15-19}) were the dominant ones as well. Such a trend indicates the impact of aquatic algae: planktonic organisms generally produce a mixture of odd chain n-alkanes, preferably C_{15}, C_{17} and C_{19}, while C_{17} is considered to be a biomarker for algae and cyanobacteria (Meyers, Ishiwatari 1993; Meyers 2003).

Terrigenous/aquatic ratio (TAR) estimates the relative contribution of terrestrial organic matter in comparison with aquatic organic matter (Bourbonniere, Meyers 1996). In the study area, the contribution of land-plant related components in comparison to that of aquatic ones was found to be increasing in the following sequence: rivers (0.69 ± 0.89) <Lagoon (1.72 ± 1.70) <Lake (3.14 ± 0.91).

Resolved aliphatic hydrocarbons/total organic carbon ratio (R/TOC) is another sensitive indicator of petroleum-pollution (Esteves *et al.* 2006), enabling to identify "hot spots" of the anthropogenic loading in the region of interest. According to this ratio, the highest anthropogenic pressure is concentrated in the Nemunas River Avandelta (L17, L18, L20; Fig. 1, Table 1) and in some specific sites of the Curonian Lagoon (L7, L12; Fig. 1). It is worth noting that significantly lower R/TOC values were detected in fine sediment from the Curonian Lagoon ($2.6 \times 10^{-4} \pm 0.7 \times 10^{-4}$ in silt) than in coarse sediment ($9.7 \times 10^{-4} \pm 11.4 \times 10^{-4}$ in sand), which is probably due to the different surface-to volume ratio of sediment particles. Riverine sand exhibited lower R/TOC values ($6.0 \times 10^{-4} \pm 5.1 \times 10^{-4}$) than those recorded in the Lagoon, while low values were obtained for silty sediment of the lake ($2.2 \times 10^{-4} \pm 0.5 \times 10^{-4}$). The results obtained suggest that even though part of the anthropogenic ALHs carried by the rivers is deposited in the Nemunas inlet area, intense hydrodynamical processes disturb their accumulation. Consequently, pollutants are carried further by the prevailing currents to the Curonian Lagoon. According to other investigations, the prevalence of petrogenic hydrocarbons is common to river estuaries (Wang *et al.* 2015).

Source evaluation/ Distribution and loadings of natural and anthropogenic ALHs

In order to evaluate sources of ALHs more precisely, the principal component analysis (PCA) was further performed using Varimax rotation as a preferable transformation technique. The data matrix was constructed with 34 sampling sites and seven column variables containing aliphatic indexes and R/TOC (Table 1). Two factors F1 and F2 were obtained, their total variances were 40%, and 35%, respectively, and the interpretation was based on geochemical marker loadings (Fig. 2).

The first rotated component F1 demonstrated significant positive ($p < 0.00001$) correlations with Pr/Ph, CPI, NAR and negative correlations with R/TOC, revealing biogenic impact increase in the positive direction of the axis and the opposite trend for anthropogenic ALHs (Fig. 2, a). A high R/TOC ratio is characteristic of highly contaminated sites (Commendatore *et al.* 2012). Increase in F1 values indicated biogenic loading with a minor contribution of anthropogenic loading.

F2 was found to be positively associated with the biogenic index, i.e. terrigenous/aquatic ratio and negatively with UCM/R and LMW/HMW, showing that the biogenic (terrigenic) character of samples is becoming more pronounced in the positive direction. On the contrary, the input of autochtonic (aquatic) organic matter was found to be growing in the negative direction of the axis. It should be added that UCM was well-defined in all of the samples studied, indicating advanced processes of weathering and biodegradation. Both UCM/R and LMW/HMW contributions were increasing in the negative direction of F2 axis and were related to contamination with light ALHs as well as to bioproduction activity (Aleksandrov *et al.* 2018).

ALHs distribution trends and differences among sampling stations were revealed by the analysis of the factor scores. Rivers (R1–R7, Fig. 1) could be distinguished by the highest amount of light and degraded hydrocarbons. High levels of UCM and even LMW hydrocarbons together with the respective geochemical markers imply that anthropogenic sources are diluted with autochthonic biogenic input. The highest contribution of terrigenous hydrocarbons was observed in the Nemunas tributary Minija (R5).

The Nemunas River Avandelta (L17, L18, L20) and station L7 demonstrated relatively fresh pollution, as the sediment collected from these locations contained a significant amount of petroleum hydrocarbons (Fig. 2, b). Abrupt changes in ALHs concentrations and composition had been observed in

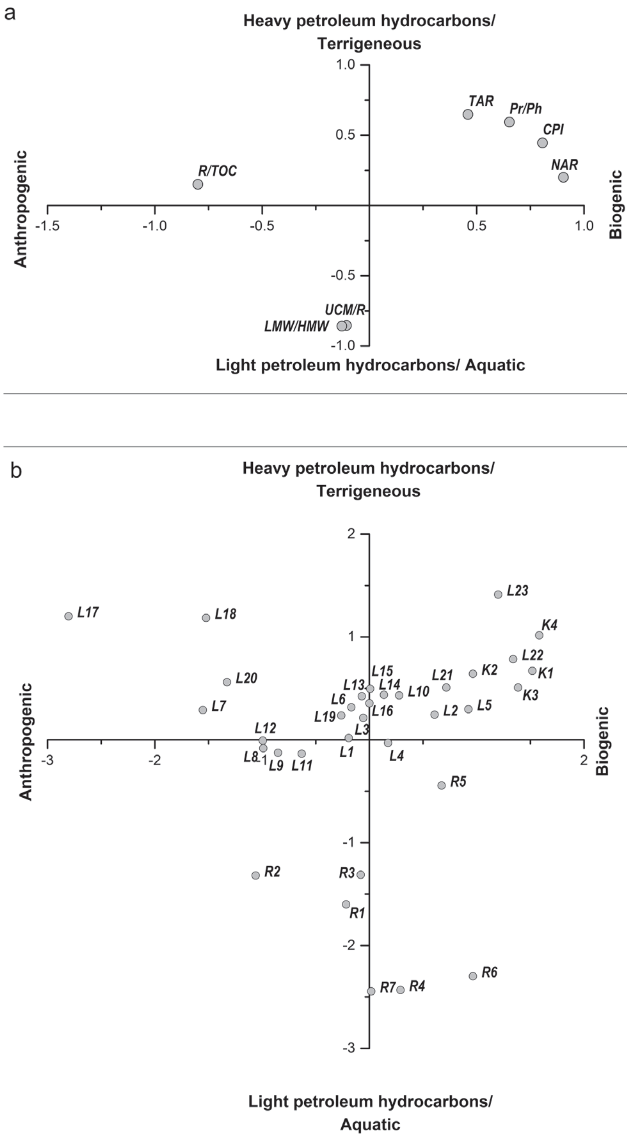

Fig. 2 Principal component analysis of hydrocarbon concentrations and aliphatic indexes: (a) Factor loadings of the aliphatic indexes (TAR, Pr/Ph, CPI, NAR, UCM/R, LMW/HMW) and R/TOC, (b) Factor score of individual sampling stations

the Avandelta region previously (Jokšas *et al.* 2003). Due to the changes in hydrodynamic processes in the barrier river-lagoon zone, part of the ALHs carried by the Nemunas River are deposited together with the coarser suspended matter fraction right in front of the river mouth in the Curonian Lagoon. HMW terrigenous hydrocarbons are more stable due to their association with plant biopolymers and waxes (Volkman *et al.* 1987) and tend to accumulate in sediment enriched with organic carbon in some undisturbed sites. Unlike natural hydrocarbons, which have strong relationships with their generic sources, anthropogenic hydrocarbons are only adsorbed onto suspended matter. They tend to fractionate easier and thus enter the sediment faster, which explains a significant contribution of anthropogenic sources in the Nemunas River Avandelta. Deposited pollutants are subsequently carried further to the Curonian Lagoon in the direction of the prevailing currents. As for station L7, a significant input of anthropogenic sources in this location is probably related to changes in hydrodynamic conditions in the fresh-salty water barrier zone (Galkus, Jokšas 1997).

On the contrary, silty sediments from the Kniaupas Bay (L22, L23) and from Lake Krokų Lanka (K1–K4) were characterized by the highest loading of biogenic, mostly terrigenous, ALHs (Fig. 2, b). Despite the well-defined UCM "hump", the dominance of odd n-alkanes implies the prevalence of natural ALHs sources diluted with anthropogenic impact. Sedimentary conditions of these relatively closed aquatories are favourable for ALHs accumulation. However, the absence of direct pollution sources resulted in the highest contribution of biogenic ALHs in the aforementioned two locations.

The indicative indexes of the remaining stations were distributed closer to the coordinate axes. Stations containing the fine sediment fraction enriched with organic carbon (L5, L10, L13–L16) exhibited higher loading of heavier ALHs and could be related to both anthropogenic and terrigenous sources. Stations L2, L4 and L21, although having less TOC, demonstrated similar trends.

It could be noted that stations located in relatively open, hydrodynamically more active sites containing coarser sediment (L1, L3, L6, L8, L9, L11, L12, L19; Fig. 1) demonstrated a slightly higher contribution of anthropogenic sources (Fig. 2, b). In addition, an unusually high input of low molecular weight ALHs, indicating the presence of aquatic sources, has also been observed at such stations. Usually, lower molecular mass ALHs produced in water do not have many chances of reaching sediment as they tend to degrade before sinking to the bottom (Volkman *et al.* 1987). However, hydrolithodynamic conditions, a steady anthropogenic pressure and intense biogenic loading might result in accumulation of lower molecular weight ALHs in sediments.

CONCLUSIONS

Hydrocarbon distribution in bottom sediments of the Curonian Lagoon and the Nemunas River Delta is affected by various hydrodynamic, morpholithodynamic and anthropogenic processes. A significant positive correlation between aliphatic hydrocarbons and fine sediment fraction has been observed in our study, organic matter content was also found to play an important role in determining the hydrocarbon distribution. ALHs concentration varied from 9.1 to 187.6 μg g^{-1} d.w. Both Lake and the rivers attributed to the Nemunas River Delta region were found to be slightly contaminated. The Curonian Lagoon could be classified as a slightly contaminated aquatory with several moderately polluted areas in the Nemunas River Avandelta, semi-enclosed bays and deeper sites.

In comparison to the results of former studies, the loading of ALHs on coarse sediments was higher. In addition, rather high concentrations of LMW hydrocarbons were recorded in coarse sediments of the Curonian Lagoon and the rivers, which could be related to both anthropogenic pressure and intense bioproductivity. The unresolved complex mixture was prevailing in all of the samples studied, indicating oil pollution and the presence of degraded/weathered hydrocarbons residues. Silty sediments from the Kniaupas Bay and from the Lake Krokų Lanka were characterized by the highest loading of biogenic, mostly terrigenous, ALHs. On the contrary, the highest loading of anthropogenic ALHs was observed in the Nemunas River Avandelta and in the fresh-salty water barrier zone in the northern part of the Curonian Lagoon.

FUNDING AND ACKNOWLEDGMENTS

This research was supported by the Open Access to research infrastructure of the Nature Research Centre under the Lithuanian open access network initiative. We would like to express our gratitude to the two anonymous reviewers of the manuscript for their valuable observations.

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