

Geochemical Markers as a Tool to Assess Sedimentary Organic Matter Sources of the Laguna Estuarine System, South Brazil: Aliphatic and Polycyclic Aromatic Hydrocarbons

Rafael Taroza,^{a,b} Morgana Frena^a and Luiz Augusto S. Madureira^{*,a}

^aDepartamento de Química, Universidade Federal de Santa Catarina,
88040-900 Florianópolis-SC, Brazil

^bDepartment of Geological Sciences, Brown University, 02912 Providence-RI, USA

Amostras de sedimentos superficiais do Sistema Estuarino de Laguna foram analisadas objetivando a identificação das fontes de matéria orgânica. Razões entre *n*-alcanos selecionados, elevados teores de hidrocarbonetos alifáticos (HA) (média de 9.168 µg g⁻¹ de carbono orgânico, CO) e policíclicos aromáticos (HPA) (média total de 426.593 ng g⁻¹ CO), e a distribuição de hopanos com estereoquímica αβ detectados nas amostras da Lagoa de Santo Antônio foram evidências de que o aporte de hidrocarbonetos petrogênicos prevalece sobre os de fontes naturais. Nas demais amostras estudadas, a distribuição de HA (de 38 até 2.749 µg g⁻¹ CO), a detecção de hopenos e hopanos-ββ sugerem hidrocarbonetos de fontes mistas. Todavia, o teor de HPA em todas as amostras (de 7.731 até 786.469 ng g⁻¹ CO, sendo que os aromáticos alquilados representaram > 92% do total) revelou contaminação petrogênica crítica. As atividades pesqueira e urbana são fontes potenciais dos hidrocarbonetos petrogênicos detectados nas amostras sedimentares.

Surface sediment samples from the Laguna Estuarine System were analyzed to identify organic matter sources. The ratios between selected *n*-alkanes, high concentrations of aliphatic hydrocarbons (AH) (average of 9,168 µg g⁻¹ of organic carbon, OC) and polycyclic aromatic hydrocarbons (PAH) (total average of 426,593 ng g⁻¹ OC), and the hopanes distribution with αβ stereochemistry found in the Santo Antônio Lagoon samples were evidence that hydrocarbon inputs from petrogenic sources predominate over natural sources. In the other samples studied, the AH distribution (from 38 to 2,749 µg g⁻¹ OC), and detection of hopenes and hopanes-ββ suggest mixed sources of hydrocarbons. Nevertheless, PAH concentrations in all samples (from 7,731 to 786,469 ng g⁻¹ OC, whereof alkyl naphthalenes accounted for > 92% of the total) indicated critical petrogenic contamination. Fishing and urban activities are potential sources to the petrogenic hydrocarbons detected in these sediment samples.

Keywords: hydrocarbons, hopanes, PAH, sediment, chromatography

Introduction

Estuaries are important areas of world's coastal zones. In general, they are highly productive and provide spawning and nursery grounds for migratory species, besides playing a significant role in the global carbon cycle.^{1,2} Furthermore, an overwhelming majority of the human populations is concentrated along or near coasts, which inevitably leads to complex problems concerning environmental quality due to the residues generated by miscellaneous human activities.

Along with various other organic and inorganic contaminants, the study of sedimentary aliphatic hydrocarbons (AH) (*e.g.*, *n*-alkanes and hopanes) provides an important tool to assess organic matter sources and pollution levels in aquatic ecosystems.³⁻⁵ This class of organic compounds has biogenic and anthropogenic sources. Natural inputs are comprised mostly of vascular plants, algae, microorganisms and early diagenesis of natural products, whereas petroleum and its derivatives are generally examples of human-related sources.^{5,6} In the case of hopanes, they appear in recent geological samples with specific stereochemistry related to their source (generally microorganisms and/

*e-mail: madureira@qmc.ufsc.br

or crude oil and its products).⁷ Moreover, due to their chemical stability and easy detectability by GC-MS, these biomarkers have been extensively used as powerful tool in petroleum and correlated studies.⁷⁻⁹ Polycyclic aromatic hydrocarbons (PAH) are also widely used in environmental research due to their persistence, ability to bioaccumulate and high toxicity (*e.g.*, mutagenic and carcinogenic effects) to any organism.^{10,11} Consequently, they have been included in the US EPA and the EU priority pollutants list.

AH and PAH enter estuarine waters via several pathways, notably from urban runoff (*e.g.*, industrial and municipal wastes, and sewage sludge), atmospheric deposition (*e.g.*, combustion of petroleum-related products, charcoal and wood), nonpoint source runoff from land and/or autochthonous sources.¹¹ Because of their hydrophobicity and low susceptibility to microbial degradation, they are readily adsorbed onto particulate matter and then buried in the bottom sediments.^{5,6} Thus, the process of distinguishing their origin in sediment is not always straightforward and requires the use of several chemical tools,⁸ which belong to the field of organic geochemistry.

The Laguna Estuarine System is one of the largest estuarine formations along the Brazilian south and southeast coasts, and is internationally known because of a communal property system where fishermen and dolphins (*Tursiops truncatus*) participate in cooperative fishing, preying on the same species, that is, mullet (*Mugil spp.*).¹² Because of the highly productive aquatic ecosystem, the town of Laguna is an important and traditional fishing port in Santa Catarina State, where some 8,000 artisanal fishermen make their living.¹³ Unfortunately, the coastal environment is also famous for the constant conflicts caused by human activities in the surrounding area. Small factories, rice culture, pig farming, urban sewage, shipping transport, and coal extraction and processing are some examples of the local pollutant sources.¹⁴

In this paper, we present the first survey of AH and PAH in surface sediments of the Laguna Estuarine System. Since the few studies carried out at this site are focused on ecological and biological aspects,^{13,15-18} this study aims to assess the AH and PAH sources and concentrations, to serve as a baseline for future monitoring programs and to improve the environmental sustainability. To achieve this goal, the separation, identification and quantification of *n*-alkanes, isoprenoid hydrocarbons, pentacyclic triterpanes and PAH were carried out. Additionally, several organic geochemical indices reported in the specialized literature were calculated in the attempt to distinguish between the diverse aliphatic and polycyclic aromatic hydrocarbons inputs and evaluate the pollution level.

Experimental

Study area and sampling

The Laguna Estuarine System, located on the southern coast of Brazil (Santa Catarina State) at *ca.* 28°25' S and 48°50' W, is composed of several lagoons with a total surface area of 220 km² (Figure S1, Supplementary Information, SI). The three main water bodies, with mean depth of 2 m (Santo Antonio, 33.85 km²; Imaruá, 86.32 km²; and Mirim, 63.77 km²), are connected one to another and to the adjacent ocean by a single narrow channel representing a choked lagoon,² where Santo Antônio Lagoon receives the main freshwater stream discharge from the Tubarão River (annual mean discharge of 50 m³ s⁻¹).¹⁴ It has been reported that the surface water salinity (ranging from 1 to 15‰) is lower than that of the bottom water (ranging from 2 to 20‰).¹⁶ In association with the frequent winds over the shallow aquatic system (81% from SW and S with annual mean velocity of 12 km h⁻¹),¹⁹ this factor plays a significant role in the input, transport, sedimentation and recycling of organic compounds.

Nine sampling sites were selected along the west side of the Laguna Estuarine System in January 2007 (Figure S1, SI). These locations were chosen because the input of coarse sediments from the near-shore coast is less expressive than on the east side. A total of thirteen surface sediment samples (0-5 cm depth) were collected as follows: Mirim Lagoon (station Mir1) - two samples (MirV: close to the margin vegetation and MirNV: 4 m from vegetation); Imaruá Lagoon (station IM1) - two samples in duplicate (IM1 and IM2); Santo Antônio Lagoon (stations SA1, SA2, SA3, SA4) - one sample *per* station; Channel site (station C1 - water course that connects Santa Marta Lagoon with the Tubarão River) - two samples in duplicate (C1 and C2); Santa Marta Lagoon (stations SM1 and SM2) - two samples in duplicate at SM1 (SM1A and SM1B) and one sample at SM2. All sediment samples were stored in glass jars (previously cleaned with 5% Extran solution, deionized water, kept at 450 °C for 4 h and rinsed with solvent), sealed with heat-treated aluminum foil-lined lids and kept frozen until being freeze-dried in the laboratory.

Analytical procedures

Prior to the laboratory work, all sediment samples were freeze-dried, pulverized with a mortar and sieved with a stainless steel sieve of 120 mesh size (<0.125 mm fraction). Homogenized subsamples from each sample were acidified with 0.1 mol L⁻¹ HCl solution to remove carbonates, rinsed with deionized water and dried at 60 °C before elemental

analysis (total organic carbon, total nitrogen and total sulfur) using a Carlo Erba EA1110 CHNS-O analyzer. Grain size analysis (clay, silt and fine sand fractions) was conducted following the procedure described by Suguio.²⁰

In order to study the sources and distribution of AH and PAH in the Estuarine System, 10 g of sediment were used. Two sets of surrogates were added to quantify the overall recovery of the aliphatic and aromatic fractions. The surrogates were deuterated hydrocarbons n -C₂₀ (n -eicosane) and n -C₃₀ (n -triacontane) for the aliphatic hydrocarbon fraction (recovery of over 80%) and p -terphenyl-d₁₄ for the aromatic fraction (recovery of over 70%).

Since molecular sulfur can interfere with GC-MS analysis, 2 g of active metallic copper was added to all samples to adsorb the sulfur during the extraction. The extractable lipids were obtained applying three successive extractions by ultra-sound. In the first step, 20 mL of dichloromethane:methanol (2:1) were used and then dichloromethane only. The extracts were combined and completely rotary evaporated. Lipids were dissolved in 3 mL of hexane and loaded into a glass column (30 cm length \times 1.3 cm i.d.) previously filled with activated silica (10 g), alumina (1 g) and metallic copper (2 g) (adapted from EPA3540C). The lipid extract was fractionated into two fractions: fraction 1 containing aliphatic hydrocarbons (F1) eluted with 55 mL of hexane, and fraction 2 with polycyclic aromatic hydrocarbons (F2) eluted with 70 mL of hexane:dichloromethane (1:1). Each fraction was rotary evaporated under nitrogen flux, concentrated to 1 mL and kept at -18 °C until analysis. Prior to the gas chromatography analysis, a known amount of deuterated n -C₁₂ (n -dodecane) ($2 \mu\text{g mL}^{-1}$) was added to F1 and a PAH deuterated solution mixture of naphthalene, acenaphthene, phenanthrene, chrysene and perylene (100 ng mL^{-1}) was added to F2 as internal standards. Individual AH were quantified by internal calibration and corrected using the response factor. External calibration was used to quantify the PAH. Hopanoids were analyzed qualitatively by comparison between samples.

The aliphatic hydrocarbon fraction was analyzed using a GC (ThermoFiningan model Trace Ultra) with injector split/splitless and flame ionization detector (FID). Injector and detector temperatures were kept at 280 and 300 °C, respectively. A Restek RTX-5 MS capillary column with 30 m \times 0.25 mm i.d. \times 0.25 μm film thickness was used. The temperature was programmed as follows: 60 °C (hold for 1.5 min) ramping at 6 °C min^{-1} to 300 °C (hold for 30 min). Splitless mode injection (1 min) was performed using 1 μL of sample extract. The carrier gas was helium at 1.5 mL min^{-1} . GC-MS analysis was carried out on a ThermoFiningan Polaris Q (ion trap as mass analyzer) interfaced to a

ThermoFiningan GC model Trace Ultra, which enabled identification of hopanoids in F1, and quantification of PAH in F2. GC conditions were as for GC/FID except that injector temperature was 250 °C and carrier gas flow was 1.0 mL min^{-1} . The MS Polaris Q was operated in full scan mode (90-500 for F1 and 50-500 Dalton for F2) and mass spectra were obtained by electron impact at 30 eV with ion source at 175 °C for F1, with values of 70 eV and 250 °C, respectively, for F2. In both cases the emission current was 250 μA and the transfer line was kept at 250 °C. Mass spectrometer parameters for F1 were optimized in order to promote less molecule fragmentation to give better relative signal for the molecular ion.⁸ For example, in the mass spectra (Figure 1) obtained with the optimal mass spectrometer parameters, the molecular ion

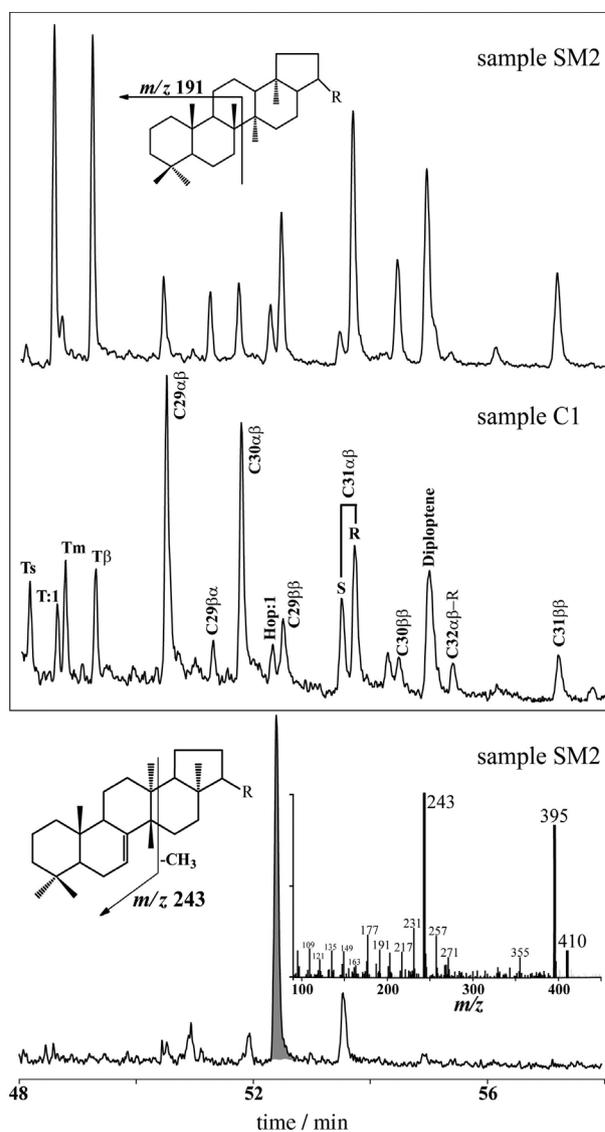


Figure 1. Example of mass chromatograms for pentacyclic triterpanes and triterpenes (m/z 191 and m/z 243) in sediments of the Laguna Estuarine System.

(m/z 410) and $[M-15]^+$ (m/z 395) peaks exhibited excellent response. When the regular mass spectrometer parameters were employed (*i.e.*, those used for F2 and widely reported in studies using the quadrupole mass analyzer), these peaks are barely seen. Xcalibur v.1.4 SR1 software was used for data acquisition and analysis.

The *n*-alkanes, isoprenoid hydrocarbons and PAH were identified by matching the retention times and fragmentation profiles against corresponding standards and those in the NIST/EPA/NIH Mass Spectra Library version 2.0d. Pentacyclic triterpanes were identified by comparison of the mass spectra obtained with those reported in the specialized literature and by analysis of a crude oil sample.^{7,9}

Results and Discussion

Grain size and elemental analysis

Surface sediment samples along the Laguna Estuarine System are comprised mostly of silt, except for stations SA3 and SM1A, where sand is the dominant sedimentary component (Table 1). Fine particles (silt and clay) have been reported to show good correlation with organic matter concentration.²¹ In this study, considering all samples (except SA3), total organic carbon showed no significant correlation with fine particles ($r = 0.483$, $p = 0.112$). However, the correlation between percentages of TOC and silt (excluding clay) was significant ($r = 0.705$, $p = 0.011$). These observations indicate that the TOC originates from nonpoint sources and winds may play an important role in

the organic matter cycle. Whitmore *et al.*²² reported that shallow, wind-stressed lakes in Florida showed highly uneven organic sediment distribution. Since the sediment samples of this study are from coastal lagoons where strong winds are frequent and human activity significant, the inputs of organic and inorganic matter are not constant. Additionally, wind waves can winnow fine particles from shoals thus modifying the texture, while tidal mechanisms have selective effects on the particle composition and size distribution.² Regarding grain particle size and TOC values, these were consistent with results previously reported for the same area.¹⁵ Table 1 shows the ratio in dry weight (dw) between TOC (total organic carbon), TN (total nitrogen) and TS (total sulfur). The TOC/TS ratio suggests that stations at Imaruf and Mirim lagoons have anoxic characteristics, considering that values lower than 3 are characteristic of anoxic environments.²³ The low water circulation observed at these sites,¹⁶ combined with small grains (only 0.2-2.4% sand) which do not contribute to sediment bioturbation by benthic fauna, could explain the tendency toward a reducing environment in the sediment. The TOC/TN ratio is used to estimate terrigenous and aquatic inputs of organic matter in aquatic environments.²⁴ The TOC/TN values (4-14) indicated mixed input of allochthonous and autochthonous organic matter.

Aliphatic hydrocarbons and *n*-alkanes

To assess the extent of pollution within the aquatic system, we analyzed chromatogram profiles and calculated several ratios between individual hydrocarbons. In addition

Table 1. Sediment characteristics, total organic carbon (TOC), total nitrogen (TN), total sulfur (TS) (percentage by dry weight) in surface sediment samples of the Laguna Estuarine System

Station	Sand / (%)	Silt / (%)	Clay / (%)	TOC / (%) ^a	TN / (%) ^a	TS / (%) ^a	TOC/TN	TOC/TS
SM2	5.0	93.8	1.2	3.74	0.49	1.41	8	3
SM1A	61.5	38.0	0.3	0.46	0.13	0.14	4	3
SM1B	18.7	80.1	1.1	3.11	0.43	1.09	7	3
C1	8.6	89.4	2.0	3.18	0.36	0.53	9	6
C2	10.6	87.7	1.7	3.14	0.35	0.49	9	6
SA1	9.4	89.1	1.5	2.66	0.22	< LOQ	12	-
SA2	44.1	55.5	0.4	0.65	0.12	< LOQ	5	-
SA3	99.9	0.1	0.0	3.39	0.24	< LOQ	14	-
SA4	33.7	65.6	0.8	0.46	0.12	0.11	4	4
IM1	0.7	96.9	2.4	1.88	0.29	1.67	6	1
IM2	0.2	97.8	1.9	1.63	0.24	1.64	7	1
MirNV	1.2	93.2	5.7	2.28	0.57	1.63	4	2
MirV	2.4	90.7	6.9	3.94	0.74	1.61	5	1

^aAverage of three replicate analyses with RSD < 10%. < LOQ: lower than limit of quantification.

to obtaining the absolute concentration values, all results (except for pentacyclic triterpanes) were normalized to TOC.

The aliphatic hydrocarbon (AH - total resolved compounds) and *n*-alkane (NA - total resolved *n*-alkanes) compositions of sediment samples have been used successfully as recorders of the origins of organic matter in coastal environments.²⁵⁻²⁹ Concentrations and indices regarding AH and NA in our samples are summarized in Table 2. The AH concentrations varied from 12.6 to 2,267.4 $\mu\text{g g}^{-1}$ of sediment dry weight (dw) and from 38.5 to 34,883.1 $\mu\text{g g}^{-1}$ of organic carbon weight (OC), whereas NA concentrations ranged from 0.9 to 45.6 $\mu\text{g g}^{-1}$ dw and from 55.1 to 7,013.5 $\mu\text{g g}^{-1}$ OC. These values are comparable to unpolluted ($< 100 \mu\text{g g}^{-1}$ dw)⁴ and polluted coastal environments around the world.³⁰⁻³² Organic carbon normalization revealed that hydrocarbon concentrations in these samples may be underestimated when expressed as dry weight, notably in SM1A (NA concentration of 4.8 $\mu\text{g g}^{-1}$ dw and 1,034.3 $\mu\text{g g}^{-1}$ OC). The Santo Antônio Lagoon samples (SA1-4) showed the highest values for both AH and NA.

Short chain *n*-alkanes were significant constituents of the total NA, ranging from 3 to 55% at the Santo Antônio stations and from 13 to 29% at the other sites. Except for SA samples, long chain odd *n*-alkanes ($n\text{-C} > 21$) were predominant with odd-to-even carbon number predominance and the most dominant compound was $n\text{-C}_{29}$ or $n\text{-C}_{31}$ (Figure 2). The NA distribution suggests that terrigenous matter and aquatic organisms are important sources of the sediments in the Laguna Estuarine System.^{5,33}

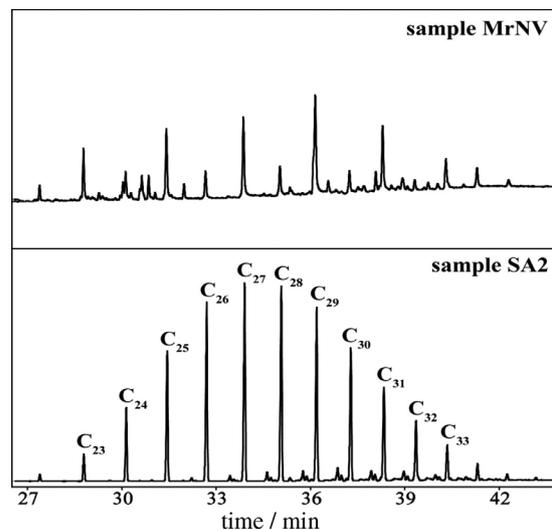


Figure 2. Chromatograms of aliphatic hydrocarbons in representative surface sediment samples of the Laguna Estuarine System. Notation: total carbon atoms in *n*-alkane chain.

This observation is supported by the above mentioned TOC/TN ratio and terrigenous/aquatic ratio (TAR - indicator of relative terrigenous *versus* aquatic organic matter input) with values ranging from 0.9 to 40.1. In contrast, samples from locations SA1-4 have profiles characteristic of petroleum derivative products with even or unimodal distribution from $n\text{-C}_{14}$ to $n\text{-C}_{34}$ showing similarities to diesel fuel chromatograms (Figure 2).³⁴ Another *n*-alkane ratio widely used in environmental studies is the Carbon Preference Index (CPI).³⁵⁻³⁷ A CPI value close to 1 suggests

Table 2. Concentrations and indices of hydrocarbons in surface sediment samples of the Laguna Estuarine System

Parameters	Stations												
	SM2	SM1A	SM1B	C1	C2	SA1	SA2	SA3	SA4	IM1	IM2	MirV	MirNV
AH / ($\mu\text{g g}^{-1}$ dw)	35.2	126.5	46.7	81.3	65.6	128.4	2,267.4	142.9	40.7	70.9	49.4	21.4	12.6
AH / ($\mu\text{g g}^{-1}$ OC)	94	2,749	150	255.6	209.6	482.9	34,883.1	421.5	884.8	377.3	303.1	42.4	38.5
NA / ($\mu\text{g g}^{-1}$ dw)	2.6	4.8	2.8	4.0	3.3	5.1	45.6	6.0	1.2	3.8	2.2	1.7	0.9
NA / ($\mu\text{g g}^{-1}$ OC)	70.8	1,034.3	90.8	127.2	104.4	192.4	7,013.5	178.4	271.7	201.8	133.5	54.5	55.1
Dominant Peak	$n\text{-C}_{29}$	$n\text{-C}_{31}$	$n\text{-C}_{31}$	$n\text{-C}_{31}$	$n\text{-C}_{31}$	$n\text{-C}_{11}$	$n\text{-C}_{27}$	$n\text{-C}_{11}$	$n\text{-C}_{20}$	$n\text{-C}_{29}$	$n\text{-C}_{29}$	$n\text{-C}_{29}$	$n\text{-C}_{29}$
UCM / ($\mu\text{g g}^{-1}$ dw)	-	107.1	-	154.8	112.0	166.1	216.1	191.3	-	43.3	29.5	11.9	6.0
UCM/NA	-	22	-	34	32	33	5	32	-	11	13	7	7
$\Sigma \text{C}_{15} - \text{C}_{20}$ / (%)	12	23	17	29	19	52	3	55	45	21	23	13	15
$n\text{-C}_{17}/\text{Pr}$	18.6	4.4	9.8	2.0	0.2	2.8	1.2	1.1	1.1	1.8	1.6	14.9	13.6
$n\text{-C}_{18}/\text{Ph}$	1.9	1.2	1.6	2.4	2.7	2.6	2.7	2.6	2.4	3.2	3.1	3.4	2.4
Pr/Ph	1.0	0.7	1.3	2.5	2.7	1.2	2.2	2.9	2.2	2.4	3.0	2.6	1.8
CPI	2.5	4.1	3.3	3.3	3.6	2.0	1.1	2.0	2.0	1.9	3.0	3.3	3.1
TAR	4.6	10.2	4.6	2.0	4.9	0.9	40.1	0.9	0.9	3.3	3.0	3.4	3.2

AH: total resolved aliphatic hydrocarbons; NA: sum of resolved *n*-alkanes from $n\text{-C}_{10}$ to $n\text{-C}_{40}$; UCM: unresolved complex mixture; Pr/Ph: pristane to phytane concentration ratio; TAR (terrigenous/aquatic ratio): $(n\text{-C}_{27}+n\text{-C}_{29}+n\text{-C}_{31})/(n\text{-C}_{15}+n\text{-C}_{17}+n\text{-C}_{19})$; CPI (carbon preference index): $2(n\text{-C}_{23}+n\text{-C}_{25}+n\text{-C}_{27}+n\text{-C}_{29}+n\text{-C}_{31})/[(n\text{-C}_{22}+n\text{-C}_{24}+n\text{-C}_{26}+n\text{-C}_{28}+n\text{-C}_{30})+(n\text{-C}_{24}+n\text{-C}_{26}+n\text{-C}_{28}+n\text{-C}_{30}+n\text{-C}_{32})]$.

the presence of petrogenic hydrocarbons and a CPI value greater than 3 suggests the presence of terrestrial plants.^{31,38} The CPI values for the sediments of this study ranged from 1.1 to 4.1 (Table 2). In addition to these results for stations SA1-4, where the lowest CPI values were found, petroleum-derived products appear as the main source of hydrocarbons. For the other samples, the CPI values suggested the influence terrigenous hydrocarbons in the sediment composition. In fact, the CPI values did not show predominance from one source, but rather indicated both anthropogenic and natural sources.

Sediment samples contaminated by petroleum products (weathered compounds or even fresh oil inputs) are known to exhibit the characteristic unresolved complex mixture (UCM) in the chromatograms of aliphatic hydrocarbons,^{8,39} although smaller contributions may be related to bacterial reworking of sedimentary organic matter.⁴ UCM was found in most of the samples with values ranging from 6.0 to 216.1 $\mu\text{g g}^{-1}\text{dw}$, which accounted for 10-85% of the AH content. Nonetheless, for samples C1, C2, SA1 and SA3 the UCM concentration was higher than that of the AH. The ratio of absolute UCM to absolute NA has been used to identify sedimentary anthropogenic hydrocarbons and values greater than 4 usually indicate petrogenic contamination.⁴⁰ Nearly all samples exhibited $\text{UCM/NA} > 11$, indicating input and/or biodegradation of fossil fuels. A recent input of fossil fuel is unquestionable in SA2, due to the value for UCM/NA, high UCM concentration and to the chromatogram profile (Figure 2). On the other hand, the UCM/NA value for samples from the Mirim Lagoon might express biodegradation of natural compounds given the low UCM concentration (6.0 and 11.9 $\mu\text{g g}^{-1}\text{dw}$) associated with low values of AH and NA.

In order to gain a better understanding of the identification of petroleum-related products, ratios between isoprenoid hydrocarbons, $n\text{-C}_{17}$ (*n*-heptadecane) and $n\text{-C}_{18}$ (*n*-octadecane) were also calculated. Pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) were detected in all samples. The origin of these branched alkanes in geological samples can be petroleum products as well as aquatic biota (*e.g.* algae and zooplankton). A high pristane (Pr) to phytane (Ph) ratio (Pr/Ph), or the predominance of a single isoprenoid (pristane), is indicative of a biogenic source⁴¹ and most crude oils have Pr/Ph values that fall within a narrow range (0.8-3).⁹ The Pr/Ph values ranged from 0.7 to 3.0 suggesting the influence of fossil fuels in all samples. The $n\text{-C}_{17}/\text{Pr}$ and $n\text{-C}_{18}/\text{Ph}$ ratios have been used in the attempt to verify weathered residues or fresh fossil fuel input to sediment samples.^{30,42} Since microorganisms generally utilize *n*-alkanes before isoprenoids, low values

for these ratios (< 1) are associated with biodegraded oil, while recent inputs may yield values greater than 1. As summarized in Table 2, the $n\text{-C}_{18}/\text{Ph}$ ratio ranged from 1.2 to 3.4 and the $n\text{-C}_{17}/\text{Pr}$ ratio varied from 0.2 to 18.6, suggesting microbial degradation of anthropogenic hydrocarbons in samples SA1-4, IM1-2, C1-2 and SM1A. It is interesting to note that high values (from 9.8 to 18.6) were found for the other samples. As discussed previously, in these samples (SM1B, SM2, MirV and MirNV), non-anthropogenic sources of hydrocarbons are predominant, thus the $n\text{-C}_{17}/\text{Pr}$ value may typify primary productivity.

Pentacyclic triterpanes

Hopanooids have been used in organic geochemical research to obtain information on recent and ancient geological environments related to organic matter maturity and oil-source rock correlations in oil exploration.^{9,43-45} These compounds originate mainly from bacterial membrane lipids (biohopanooids, *e.g.*, bacteriohopanetetrol) and once the bacteria are buried in sediments, diagenetic processes readily modify their structure leading to the formation of geohopanooids, including pentacyclic triterpanes (mostly hopenes and hopanes) and other compounds with different functional groups.^{7,9,46} Recently buried hopanes found in modern sediments (with no or a very low degree of maturation) generally have $17\beta(\text{H}), 21\beta(\text{H})$ stereochemistry and occur only in the R configuration at the C_{22} position in extended-molecules, whereas ancient buried hopanes (higher degree of maturation, *e.g.*, found in petroleum) are identified by the $17\alpha(\text{H}), 21\beta(\text{H})$ configuration (more thermodynamically stable) associated with the R and S epimers at the C_{22} position, which do not occur in living organisms.^{7,9,47} Environmental researchers have taken advantage of these very specific stereochemical changes using the hopanes series (27 to 35 carbon atoms) with the $17\alpha(\text{H}), 21\beta(\text{H})$ configuration and epimers (R and S) as additional evidence of petrogenic pollution in the aquatic ecosystems.

We found the hopane series $\text{C}_{27}\text{-C}_{32}$ (except C_{28}) in all samples. Hopenes were also detected. Their relative distribution in the lagoons were normalized by the total relative amount found in sample C1 (sample with the highest percentage of hopanes), as summarized in Table 3. The representative mass chromatograms (m/z 191 and m/z 243) and basic chemical structures are given in Figure 1. Fernene was detected (by monitoring m/z 243) in most samples with a higher relative percentage at the sites next to the vegetated margin (2.0, 8.9, 1.7 and 1.8% for SM2, C1, C2 and MirNV, respectively). Marsh plants are the predominant vegetation on the west side of the estuary (where all samples

Table 3. Relative distribution of pentacyclic triperpanes and triterpenes in surface sediments and selected individual compound ratios

Hopanoids and ratios	Symbol	Stations													
		SM2	SM1A	SM1B	C1	C2	SA1	SA2	SA3	SA4	IM1	IM2	MirNV	MirV	
18 α (H)-22,29,30-Trisnorneohopane	Ts	< S/N	< S/N	< S/N	3.4	0.5	< S/N								
22,29,30-Trisnorhop-17(21)-ene	T:1	7.1	0.3	2.4	5.5	0.6	0.4	-	0.3	-	1.5	2.9	1.8	1.6	
17 α (H)-22,29,30-Trisnorhopane	Tm	0.7	-	0.4	5.0	0.7	0.7	-	0.5	-	0.3	0.4	0.3	0.3	
17 β (H)-22,29,30-Trisnorhopane	T β	5.5	0.6	3.7	5.6	0.9	0.6	-	0.4	-	0.9	1.4	1.7	2.0	
17 α (H),21 β (H)-30-Norhopane	C29 $\alpha\beta$	1.8	-	-	18.7	2.8	1.6	0.5	1.4	0.3	0.8	0.9	0.8	0.9	
17 β (H),21 α (H)-29-Normoretane	C29 $\beta\alpha$	1.5	-	1.0	3.2	0.5	0.4	-	0.2	-	0.2	0.4	0.4	0.7	
17 α (H),21 β (H)-Hopane	C30 $\alpha\beta$	1.7	-	1.2	16.3	2.3	2.0	0.7	1.5	0.4	0.9	1.0	0.6	0.8	
Hopene	Hop:1	1.4	-	1.2	-	-	0.4	-	-	-	0.4	0.4	0.4	0.5	
Fernene		2.0	0.2	1.4	8.9	1.7	0.5	-	0.2	-	0.3	0.5	1.2	1.8	
17 β (H),21 β (H)-30-Norhopane;	C29 $\beta\beta$	3.6	0.3	2.2	4.1		0.4	-	0.4	-	0.7	1.2	1.1	1.4	
17 α (H),21 β (H)-31-Homohopane-22S	C31 $\alpha\beta$ -S	1.0	-	0.5	5.7	1.3	1.0	0.4	0.6	-	0.3	0.5		0.3	
17 α (H),21 β (H)-31-Homohopane-22R	C31 $\alpha\beta$ -R	6.7	0.6	4.3	8.8	1.5	1.1	0.3	0.6	-	0.8	1.1	1.3	1.8	
17 β (H),21 β (H)-Hopane	C30 $\beta\beta$	2.7	-	1.8	0.0	-	-	-	-	-	0.5	0.8	1.2	1.6	
Hop-22(29)-ene (diploptene)		6.6	-	3.4	12.5	2.4	-	-	-	-	0.7	1.5	1.4	2.0	
17 α (H),21 β (H)-32-Bishomohopane-22S	C32 $\alpha\beta$ -S	-	-	-	-	-	1.1	-	0.7	-	-	-	-	-	
17 α (H),21 β (H)-32-Bishomohopane-22R	C32 $\alpha\beta$ -R	-	-	-	0.6	-	0.3	-	0.2	-	-	-	-	-	
17 β (H),21 β (H)-31-Homohopane	C31 $\beta\beta$	3.2	-	-	2.2	0.5	0.6	-	0.3	-	0.8	1.2	1.2	2.1	
Total / (%)		45.4	1.9	23.4	100	15.1	11.0	1.9	7.3	0.7	8.7	14.3	13.8	18.6	
Ts/(Ts+Tm)		-	-	-	0.40	0.45	-	-	-	-	-	-	-	-	
T β /(Ts+Tm)		8.4	-	9.5	0.67	0.73	0.82	-	0.68	-	3.4	3.2	6.5	7.4	
22S/(22R+22S) $\alpha\beta$ C31		0.13	-	0.10	0.39	0.46	0.47	0.56	0.49	-	0.28	0.31	-	0.16	
22S/(22R+22S) $\alpha\beta$ C32		-	-	-	-	-	0.77	-	0.73	-	-	-	-	-	

< S/N: signal lower than signal to noise ratio of 3.

were collected). To the best our knowledge, there have been no reports indicating the marshes or petroleum as a possible source of fernene. Hence, this biomarker is more likely derived from microbiotic precursors.⁴⁸ Diploptene (present in various types of bacteria)⁴⁹ and its possible diagenetic products (other hopenes) were detected in all samples (monitoring *m/z* 191 and 189) following the same trend as that observed for fernene, and thus supporting the hypothesis of a biogenic source for this compound. The hopane skeleton with the configuration 17 β (H),21 β (H) was dominant in samples from the Santa Marta, Imaruf and Mirim Lagoons. On the other hand, 17 α (H),21 β (H)-30-norhopane and 17 α (H),21 β (H)-hopane were dominant in the sediment samples C1 and C2 and SA1, 2, 3, and 4. Besides the use of the identification of the hopane series with specific stereochemistry and epimers to verify petroleum residues, several ratios have been applied to

estimate the degree of maturity of sedimentary organic matter. The ratios of 18 α (H)-22,29,30-trisnorneohopane (Ts) to 17 α (H)-22,29,30-trisnorhopane (Tm) (Ts/Ts+Tm) and of the S to R epimers of 17 α (H),21 β (H)-homohopane and 17 α (H),21 β (H)-bishomohopane (22S/22S+22R) have been used to assess changes during the maturation of the sedimentary organic matter. Tm and the biological epimer 22R (both thermodynamically less stable than Ts and the geological epimer 22S, respectively) are affected by sediment maturity and the ratio values increases from 0 to ca. 0.6 during maturation.^{7,9} The results of these ratios are given in Table 3.

The relative percentages of the recent pentacyclic triterpanes (mainly indicative of biogenic sources: hopenes, hopanes- $\beta\beta$, and C31 $\alpha\beta$ -R) and ancient pentacyclic triterpanes (mainly indicative of petrogenic sources: hopanes- $\alpha\beta$, including the epimer C31 $\alpha\beta$ -S), are shown

in Figure 3 (we excluded C32 $\alpha\beta$ and epimers because of their low frequency). Biomarkers characteristic of biogenic precursors ranged from 84% to 100% in the Santa Marta and Mirim Lagoons. Considering the low levels of AH, NA and UCM (excepted for SM1A) associated with low 22S/(22R+22S) ratios for C₃₁ $\alpha\beta$ (from 0.105 to 0.155), the contribution of petrogenic sources to the sedimentary organic matter is small compared to highly contaminated samples (*e.g.*, SA1-4). A 17 α (H),21 β (H) and 22S/(22R+22S) ratio for C₃₁ $\alpha\beta$ (0.277 and 0.307) was observed in the samples IM1 and IM2. Petrogenic-related hopanes ranged from 51 to 100% in the Santo Antonio Lagoon. The 22S/(22R+22S) ratio values for C₃₁ $\alpha\beta$ (from 0.277 to 0.467) and C₃₂ $\alpha\beta$ (0.766 and 0.733) are indicative of petrogenic input.^{9,50} Diesel and gasoline are excluded as possible sources since they belong to the low boiling point fraction of crude oil, which does not contain hopanes.^{51,52} Other petroleum-related products, such as lubricating oils and marine diesel may be potential sources. The relative distribution of hopanes and hopenes in samples C1 and C2, associated with the 22S/(22R+22S) ratio for C₃₁ $\alpha\beta$ (0.393 and 0.465) and Ts/(Ts+Tm) ratio (0.404 and 0.452) indicated mixed sources (biogenic and anthropogenic).

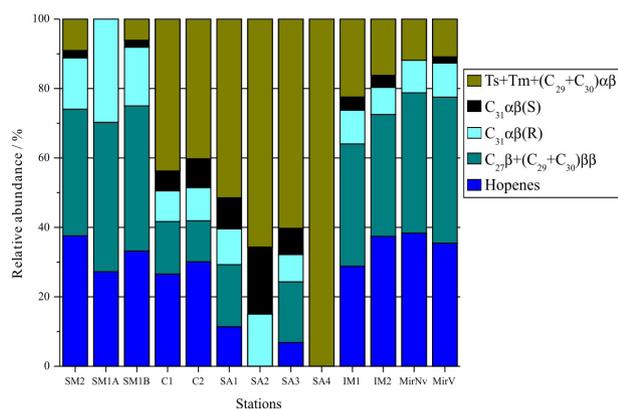


Figure 3. Relative distribution of biogenic-related (hopenes, hopanes- $\beta\beta$, C₃₁ $\alpha\beta$ -R) and anthropogenic-related (Ts, Tm, hopanes- $\alpha\beta$, C₃₁ $\alpha\beta$ -S) pentacyclic triterpanes and triterpenes.

17 β (H)-22,29,30-Trisnorhopane (T β) was detected in most samples. Tm has been reported to be thermodynamically less stable than Ts during catagenesis and thus the Ts/(Ts+Tm) ratio is a maturity indicator in oil studies.⁹ T β shows even lower thermal stability⁹ and thus we propose that the T β /(Ts+Tm) ratio may be related to a pentacyclic triterpane source. Based on the organic geochemical parameters discussed above, we suggest that in these study values of this ratio of > 6 indicate significant biogenic input (bacterial), values < 6 and > 1 indicate mixed sources, and values < 1 indicate predominance of petrogenic sources (Table 3).

Polycyclic aromatic hydrocarbons

In order to gain further insight into anthropogenic influences on the superficial sediments of the Laguna Estuarine System, polycyclic aromatic hydrocarbons (PAH) analysis was carried out by GC-MS. The biogeochemistry of PAH in ecosystems is well documented, and likewise their source-indicator parameters have been widely used in atmospheric, aquatic and sedimentary studies.^{3,4,26,52-59}

PAH were identified and quantified in all samples (Table 4). The total of 18 individual PAH (including parent and the sum of individual alkylated compounds) ranged from 1,107 to 250,094 ng g⁻¹ dw and from 6,719 to 786,460 ng g⁻¹ OC. Again, organic carbon normalization was necessary to verify whether the PAH concentrations were underestimated (*e.g.*, SM1A and IM2) when expressed as dry weight. Our values are comparable or higher than those previously reported for highly polluted coastal areas worldwide (*e.g.*, Guanabara bay, Brazil, up to 9,700 ng g⁻¹ dw; Cienfuegos bay, Cuba, up to 10,500 ng g⁻¹ dw; Patos Lagoon, Brazil, up to 11,779 ng g⁻¹ dw; Narragansett Bay, USA, up to 216,000 ng g⁻¹ dw.).^{3,31,60,61} PAH distribution was dominated by alkylated compounds, notably alkyl-naphthalenes. The Santo Antônio Lagoon and Channel samples exhibited the highest PAH concentrations, whereas the lowest concentrations were found in the Santa Marta and Mirim Lagoons with the exception of sample SM1 (organic carbon normalization revealed a 22-fold increase, which is much higher than the average (3-fold) for the samples from that location). Alkyl PAH accounted for \geq 92.4% of total PAH at all sites, which indicates a strong influence of fossil fuels on the sediments.⁵³ Further data analysis considering the estuarine and marine sediment quality guidelines specified by US NOAA (National Oceanic and Atmospheric Administration - United States Department of Commerce)⁶² demonstrated that the total PAH concentration of the sediment samples from Santa Marta and Mirim Lagoons (averages of 2,357 and 2,423 ng g⁻¹ dw, respectively) are below the effects range-low (ERL) value of 4,022 ng g⁻¹ dw (a range intended to estimate conditions in which adverse biological effects would be rarely observed), whereas the Imaruí Lagoon sediments (total average PAH of 17,258 ng g⁻¹ dw) had a value between the ERL and effects range-median (ERM) (value of 44,792 ng g⁻¹ dw, which represents a probable-effects range within which adverse biological effects would frequently occur) representing a possible-effects range with adverse biological effects would occasionally occur. In the Santa Marta and Imaruí Lagoons the total alkyl-naphthalenes are above the ERM value of 670 ng g⁻¹ dw for 2-methyl naphthalene. In contrast, the total PAH concentration at the Santo Antônio Lagoon and Channel stations (average of

Table 4. Analytical data and selected individual compound ratios for PAH

PAH	Stations												
	SM2	SM1A	SM1B	C1	C2	SA1	SA2	SA3	SA4	IM1	IM2	MirNV	MirV
Naphthalene (Naph) ^a	21.1	5.4	13.2	587.9	36.1	172.2	79.3	179.7	44.5	39.6	38.0	14.1	16.9
∑ Alkyl-naphthalenes ^a	2,650.4	976.8	2,756.1	243,845.6	16,441.0	79,560.5	39,239.8	85,359.8	20,065.6	13,981.7	17,703.7	1,915.4	2,437.5
Fluorene (Fl) ^a	5.5	4.0	9.7	196.7	55.2	179.2	5.4	204.0	54.1	31.5	41.2	8.2	6.2
∑ Alkyl-fluorenes ^a	10.3	9.1	16.0	238.1	104.6	323.8	101.5	325.7	93.0	40.7	56.2	12.3	12.0
Dibenzothiophene (Dbt) ^a	3.3	1.9	2.6	52.4	21.1	62.8	5.0	99.2	23.1	15.7	21.1	2.6	1.6
∑ Alkyl-dibenzothiophenes ^a	2.4	0.0	0.0	121.4	80.3	128.6	26.1	207.4	60.4	32.2	36.8	2.6	6.4
Phenanthrene (Phe) ^a	18.9	11.0	31.4	696.0	225.3	619.6	187.6	678.8	182.8	108.4	144.6	23.9	16.6
∑ Alkyl-phenanthrenes ^a	52.0	26.6	86.7	1,531.8	698.0	2,000.1	617.0	2,017.8	530.1	314.6	423.1	53.9	72.9
Anthracene (Ant) ^a	4.8	2.4	8.2	128.5	77.6	157.5	43.3	148.2	40.1	20.5	27.8	4.4	3.1
Fluoranthene (Flt) ^a	1.2	1.1	1.6	-	-	-	-	-	-	-	-	-	-
Pyrene (Py) ^a	8.0	3.0	15.3	109.5	47.6	121.3	34.6	121.0	35.6	34.4	35.3	14.9	8.6
∑ Alkyl-pyrenes ^a	42.9	10.4	68.4	699.3	436.1	1295.2	366.9	1235.2	337.3	243.5	287.9	16.6	26.2
Benzo[a]anthracene (BaA) ^a	21.3	3.9	22.5	346.4	211.4	595.4	169.8	556.7	158.6	122.9	141.8	6.8	8.1
Chrysene (Chy) ^a	8.2	5.0	14.3	49.6	41.0	93.8	31.0	105.3	23.5	26.7	24.7	10.0	8.3
Benzo[b]fluoranthene (BbF) ^a	19.6	6.8	38.1	247.7	128.6	353.7	110.1	337.2	94.6	68.7	83.1	15.7	11.6
Benzo[k]fluoranthene (BkF) ^a	11.6	-	-	348.3	129.9	318.7	72.6	258.3	77.7	59.9	82.1	27.9	20.2
Benzo[a]pyrene (BaP) ^a	4.9	20.1	-	511.6	180.6	455.4	129.3	411.9	117.5	90.0	105.3	24.3	22.9
Benzo[g,h,i]perylene (BgP) ^a	21.4	25.0	-	197.4	71.7	181.1	51.5	95.3	29.6	41.5	42.8	14.1	1.7
∑ Total PAH ^a	2,891	1,107	3,074	250,094	18,947	86,433	41,194	92,094	21,894	15,258	19,258	2,647	2,198
∑ Total PAH (ng g ⁻¹ OC)	7,731	24,071	9,883	786,460	60,503	324,993	633,749	271,665	475,964	81,159	118,150	6,719	9,641
∑ Total Alkyl-PAH / (%)	95.4	92.4	95.2	98.5	93.7	96.4	98.0	96.8	96.3	95.8	96.1	92.5	95.3
∑ Alkyl Phe/Phe	2.8	2.4	2.8	2.2	3.1	3.2	3.3	3.0	2.9	2.9	2.9	3.3	3.1
Phe/Ant	3.9	4.6	3.8	5.4	2.9	3.9	4.3	4.6	4.6	5.3	5.2	5.4	5.4
BaA/Chr	2.6	0.8	1.6	7.9	5.9	6.4	5.5	5.3	6.8	4.6	5.7	0.7	1.0

^aConcentration expressed as ng g⁻¹dw.

134,521 and 60,404 ng g⁻¹ dw, respectively) are far above of the ERM value.

In an attempt to differentiate petrogenic from pyrogenic PAH, the concentration ratios of selected PAH were calculated as follows: phenanthrene/anthracene (Phe/Ant), sum of alkyl phenanthrenes/phenanthrene (∑alkyl-Phe/Phe) and benzo[a]anthracene/chrysene (BaA/Chy). Characteristic values of these ratios indicate: (i) petrogenic sources: > 15, > 2 and ≤ 0.4, respectively; and (ii) pyrolytic sources: < 10, < 2 and > 0.9, respectively.⁴ The results for all samples (Table 4) were: Phe/Ant < 10, ∑alkyl-Phe/Phe > 2 and BaA/Chy > 0.7 suggesting mixed PAH origins in the sediments of the Laguna Estuarine System, where liquid fossil fuels (direct inputs) and combustion (atmospheric deposition) of hydrocarbon-based fuels (e.g., gasoline, diesel, oil, wood and coal) are potential sources.^{4,53} According to this information, petroleum-related products have widespread presence in the sediments of the estuary, differing only in terms of concentration.

Conclusions

The uneven surface distribution of sand, silt and clay along the shallow Laguna Estuarine System and the lack

of a linear relationship between clay and TOC indicate that winds, natural water sources and human activities play a significant role in sediment transport and organic matter geochemical cycling. Also, this investigation showed that even though they are interconnected, the lagoons have significantly different sources and concentrations of sedimentary organic compounds. The lowest anthropogenic influence was verified at Mirim Lagoon. At this sampling station, the aliphatic hydrocarbon fraction was comprised mostly of natural sources, although the PAH levels and ratios indicated high contamination levels. Elevated levels of hydrocarbons in the other sediment samples and the geochemical markers revealed anthropogenic input of petroleum-related products to the aquatic system, especially the Santo Antonio Lagoon and the Channel. The data obtained also suggest that the Tβ/(Ts+Tm) ratio is a potential tool to estimate hopane sources in recent sediments.

Considering all samples studied, a comparison of the PAH concentrations in the estuarine sediments with quality guidelines specified by US NOAA revealed serious levels of petrogenic pollution across the entire aquatic system. Further research to assess the adverse effects on the biota

is needed to better understand the significance of the pollutants present in these coastal lagoons.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbcq.org.br>, as PDF file.

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Geochemical Markers as a Tool to Assess Sedimentary Organic Matter Sources of the Laguna Estuarine System, South Brazil: Aliphatic and Polycyclic Aromatic Hydrocarbons

Rafael Taroza,^{a,b} Morgana Frena^a and Luiz Augusto S. Madureira^{*,a}

^aDepartamento de Química, Universidade Federal de Santa Catarina,
88040-900 Florianópolis-SC, Brazil

^bDepartment of Geological Sciences, Brown University, 02912 Providence-RI, USA

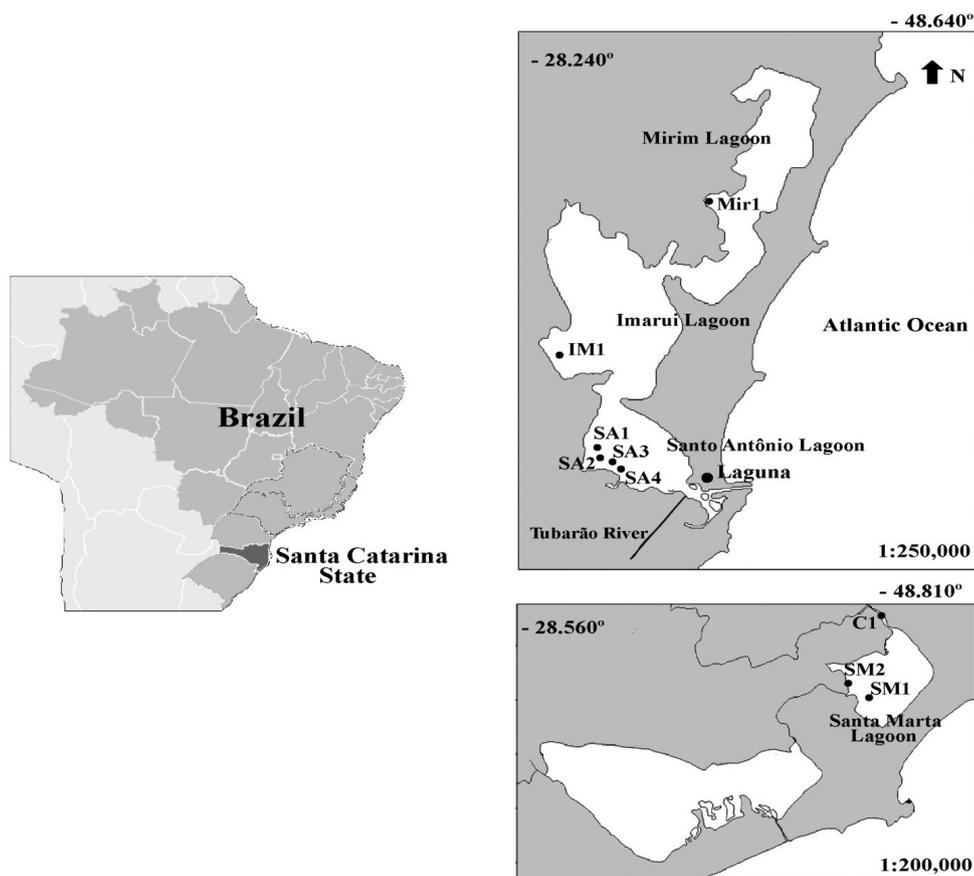


Figure S1. Map of the sampling stations in the Laguna Estuarine System.

*e-mail: madureira@qmc.ufsc.br