Baseline

Distribution and sources of aliphatic hydrocarbons in surface sediments of Sergipe River estuarine system

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ABSTRACT

The assessment of aliphatic hydrocarbons was performed in the Sergipe River estuarine system, northeastern Brazil. Aliphatic hydrocarbons concentration ranged from 9.9 ug g^{-1} up to 30.8 ug g^{-1} of dry sediment. The carbon preference index (CPI, based on nC_{24} to nC_{34} range), indicated predominance of petrogenic input in two of the sites analyzed (P4 and P5). The unresolved complex mixture (UCM) was found to be present in seven of the nine sites sampled (except for P4 and P5). Overall, the results of this work suggest that there is a mix of organic matter sources to the sediment. Although the coast of Sergipe has an intense off shore petroleum exploration and the Sergipe River crosses the entire city of Aracaju, the capital city of Sergipe, non-significant anthropogenic fingerprint was assessed.

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Coastal environments, such as rivers, lagoons and estuaries, are very important areas for recreational and industrial activities for the people living in these areas. Riverine sediments, as well as marine sediments in coastal zones, serve as an ultimate reservoir for natural and anthropogenic organic matter generated by organisms living in them and the overlying water column, supplied specially by the river discharge (Raymond and Bauer, 2001; Gao et al., 2007; Maioli et al., 2010a).

Aliphatic hydrocarbons are considered to be one of the most abundant components of organic material and one of the major classes of organic compounds found in sediments of estuarine environments (Asia et al., 2009; Maioli et al., 2010a). A high abundance of aliphatic hydrocarbons is a potential source of pollution and may cause adverse effects on marine life (Macias-Zamora, 1996). Despite of their anthropogenic sources, aliphatic hydrocarbons have also several natural sources, such as terrestrial plant waxes, marine phytoplankton and bacteria, biomass combustion and diagenetic transformation of biogenic precursors (Maioli et al., 2010b).

Moreover, sedimentary aliphatic hydrocarbons have received special attention because these compounds are readily adsorbed onto particulate matter, which will eventually sink. Therefore, bottom sediments may act as source of these possible contaminants (Medeiros et al., 2005). Because of these characteristics and sources, studies involving aliphatic hydrocarbons assessment have used indexes and ratios to distinguish between inputs and evaluate their ecological impacts (Macias-Zamora, 1996; Silva et al., 2008; Hu et al., 2009; Tarozo et al., 2010). Based on their distribution,

odd-over-even aliphatic hydrocarbons predominance will mainly represent inputs of algae, bacteria and vascular plants (Silva et al., 2008). On the other hand, a distribution with no odd-over-even predominance will reflect more mature organic matter, characteristics of petroleum hydrocarbons.

Among the tools for hydrocarbon source assessment, the carbon preference index (CPI), a numerical means of representing the odd-over-even predominance in aliphatic hydrocarbons in a particular carbon-number range, is frequently used (Commendatore and Esteves, 2004). The amount of unresolved complex mixture (UCM) is also useful for source determination. UCM is a complex mixture, normally associated with petroleum hydrocarbons distribution, which is not resolved during gas chromatography analysis and appears as a hump in the chromatogram (Killops and Killops, 2005). Terrestrial and aquatic hydrocarbons ratio (TAR) helps to determine the main source of hydrocarbons, if allochthonous or autochthonous. The total organic carbon (TOC) can be associated with local productivity (Silva et al., 2008).

Sergipe River estuarine system has been subject to urban and industrial inputs, mostly coming from Aracaju, the capital city of Sergipe. Also, Sergipe has a history of petroleum exploration of more than 50 years, both on-shore and off-shore. Despite of intense anthropogenic activities surrounding the Sergipe River, no data on aliphatic hydrocarbons distribution have been assessed in the water, particulate matter or sediment. Therefore, the aim of this study was, for the first time, to evaluate the amount and distribution of aliphatic hydrocarbons in surface sediments of Sergipe River estuarine system.

This estuarine system is composed by the main affluent, Sergipe River, together with Poxim and Sal River (Fig. 1). It is surrounded by intense industrial and urban activities, being well represented

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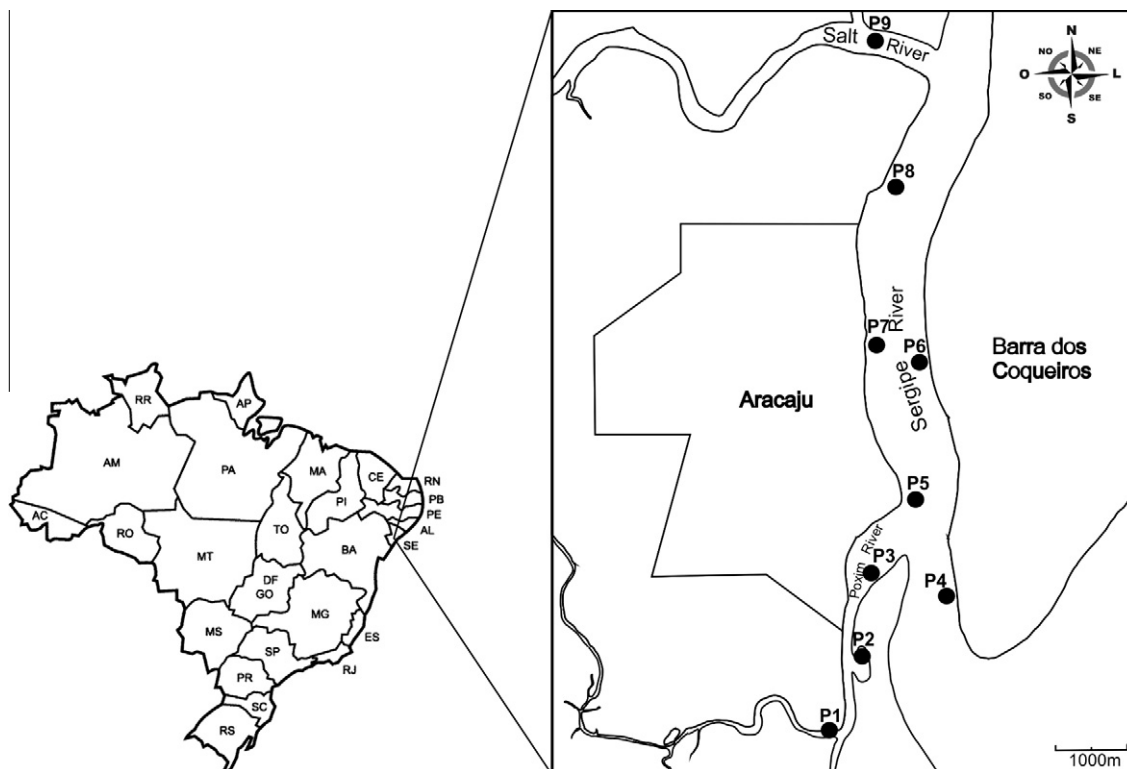 E-mail address: mralexandre@ufs.br (M.R. Alexandre).

Fig. 1. Map of the sampling sites.

by the offshore petroleum exploration, which is the third in the Brazilian ranking of producers (ANP, 2010). The total population living in the area is near 890.000 inhabitants, representing over 43% of the Sergipe population (IBGE, 2010). The climate is predominantly semi-arid with average temperature of 26 °C. It has a dry summer extending from August to February and a rainy winter.

A total of nine samples were collected after the rainy season in 2010. The sampling sites (Fig. 1) were chosen within ten kilometers of saline intrusion. They were chosen to contemplate both urban inputs and petroleum exploration susceptibility. Surface sediments samples (0–10 cm) were collected with a stainless-steel dredge sampler and kept in pre-cleaned glass container with aluminum foil protected lid. At the sampling site, samples were homogenized and one milliliter of chloroform was added to the samples to avoid microbiological degradation. Once in the laboratory, they were kept in the refrigerator. After lyophilization, samples were ground using a mortar and pistil, extracted and analyzed.

About 4 g of lyophilized and ground sediment was extracted by ultrasonication with 8 mL of dichloromethane for 30 min. The sample was then centrifuged, the dichloromethane was collected and the procedure was repeated two more times. Pieces of activated cooper were added to each extraction to remove sulfur. The organic extracts were combined and concentrated, first in rotary evaporator at 40 °C, followed by a gentle nitrogen stream. The concentrated extract was fractionated using an activated silica-gel/neutral alumina column (2 g of silica-gel and 1 g of neutral alumina; column size 13 × 1 cm). The aliphatic hydrocarbons fraction (HFr) was recovered using 8 mL of hexane. The HFr was then concentrated using nitrogen stream, spiked with internal standard (hexadecane deuterated – nC_{16}) and subjected to GC-FID and GC–MS analysis (Alexandre et al., 2006; Maioli et al., 2011).

All solvents used were HPLC grade (J.T. Baker). Certified standards were purchased from Sigma–Aldrich (St. Louis, MO, USA) at purities greater than 95%. Working solutions were prepared by dilution to appropriated concentration. Silica-gel (60–200 μm)

from Silicyle (Quebec City, Canada) and neutral alumina (50–200 μm) from Sorbent Tech (Norcross, GA, USA) were activated at 120 °C for 48 h and kept in dissector until usage. Adsorption columns were packed using dichloromethane, which was changed for hexane prior fractionation.

In order to evaluate the qualitative distribution of aliphatic hydrocarbons, analyses were performed on a Shimadzu GC–MS QP2010Plus (Kyoto, Japan), equipped with split/splitless injector and a capillary column DB5-MS (30 m × 0.25 mm and 0.25 μm of film thickness) supplied by J.W. Scientific (Santa Clara, CA, USA). The injection was performed in splitless (1 min) mode, at 300 °C, using an AOC-20i automatic injector. The column temperature ranged from 40 °C for 1 min up to 310 °C at 10 °C min⁻¹, being held at final temperature for 19 min. The injection port and the GC–MS interface were kept at 300 °C. Helium (99.995%) was used as the carrier gas, at 1.20 mL min⁻¹. The data were acquired and processed using the Shimadzu GC Solution software. Analysis were performed in the SCAN mode (mass interval of 40 and 600 Da). The ion source was operated at 70 eV and 200 °C of temperature.

The quantitative evaluation was performed using a Shimadzu GC-FID 2010, with the same settings as for GC–MS. The column was a DB5-MS (30 m × 0.25 mm and 0.25 μm of film thickness) capillary column. Nitrogen (30 mL min⁻¹) was used as make up gas, Helium as carrier and Air:Hydrogen ratios was 400:40 mL min⁻¹.

Quality assurance procedures included analytical blank control, recovery control and calibration curves checking prior analysis. The highest detection limit (0.003 μg g⁻¹) was found for compounds between nC_{10} and nC_{19} and for nC_{36} up to nC_{40}. Limit of quantification ranged from 0.003 μg g⁻¹ for nC_{18} and nC_{20} throughout nC_{35}; and 0.05 μg g⁻¹ for nC_{36} up to nC_{39}. Recovery values ranged from 81.2% to 119.5% for all compounds in two fortification levels (0.5 μg mL⁻¹ and 4.0 μg mL⁻¹).

Samples for total organic carbon (TOC) and total nitrogen (TN) were first treated with 0.1 mol L⁻¹ HCl solution to remove

carbonate and analyzed using a ThermoFinnigan (Yokohama, Japan) FlashEA 1112 Series elemental analyzer.

The distribution of sedimentary aliphatic hydrocarbons is mostly controlled by the amount of fine fraction (<63 µm) and the total organic carbon associated with the deposition site. Table 1 shows some of the characteristics of the sediment samples. The TOC concentrations ranged from 0.1% (P4) up to 3.2% (P6). These values are well consistent for estuarine systems (Darilmaz and Kucuksezgin, 2007; Maioli et al., 2010b; Martins et al., 2011). The total organic matter (TOM) is well correlated with TOC (>0.9), and both data are poorly associated with the silt–clay fraction (<0.6), which ranged from 0.2% at site P4 up to 35.5% at site P5. It has been demonstrated that organic matter has strong affinity for sedimentary fine particles (Mater et al., 2004). However, the results herein have shown no correlation between organic matter and fine particles (silt and clay). This find may be indicative of an important role that hydrodynamic plays in riverine estuarine systems, allowing non regular organic matter deposition with non preference for fine particles.

Although bulk TOC/TN ratio does not identify the source of organic matter in sediments, it is accepted that autochthonous inputs have low TOC/TN values, while land derivate organic matter presents high values (Killops and Killops, 2005). The results found in this study suggest massive allochthonous inputs to the sediments. Values for TN were only detected in 4 samples (P2, P5, P6 and P7), with given value for TOC/TN ratio higher than 15.6 and up to 270.3 (Table 1).

The organic matter (OM) in sediments may come from algae, aquatic plants, plants surrounding the system, organisms present in the water column or associated with eroded soil as well as anthropogenic inputs. Because of their low susceptibility to microbial degradation relative to others compounds present in the OM, aliphatic hydrocarbons in sediments are generally robust records of OM origin (Silva et al., 2008).

The total concentration of aliphatic hydrocarbons found in this study is given in Table 1. The sum of linear or n-aliphatic hydrocarbons was found to be in the range of 9.9 µg g^{-1} and 30.8 µg g^{-1} for station P9 and P6, respectively. Linear aliphatic hydrocarbons, despite their natural sources, are frequently associated with petroleum contamination. This contamination may occur from direct deposition in the sediments or indirect means such as land run off. For decades, the amount of hydrocarbons in marine ecosystems has been of concern (Anderlini et al., 1981; Macias-Zamora, 1996; Tarozo et al., 2010). In this study, the values are comparable to the amount found in the Coast of Baja California [average of 14.9 µg g^{-1} (Macias-Zamora, 1996)], in Laguna Mar Chiquita [13.2 µg g^{-1} in the first 15 cm (Silva et al., 2008)], and in Laguna Estuarine System [average of 6.4 µg g^{-1} (Tarozo et al., 2010)]; these ecosystems are known to be under intense anthropogenic influence, specially due their proximity to large cities and agricultural activities. However, according to Zegouagh et al. (1998) and Silva et al. (2008), the results found here may be considered typical of uncontaminated surface sediments, where values should be lower than 50 µg g^{-1} of dry sediment.

Samples from sites P4 and P5 presented nC_{15} as the major homologous (nC_{max}) in the n-alkane distribution, while for the others, nC_{max} was the nC_{29}, typical of terrestrial plants (Fig. 2). These finds are in agreement with TAR [terrestrial to aquatic ratio = $[(nC_{27} + nC_{29} + nC_{31})/(nC_{15} + nC_{17} + nC_{19})]$, which indicates terrigenous inputs to the sediments when values are higher than 1. The ratio of low molecular weight to high molecular weight (LMW/HMW) corroborate with the indicative of terrestrial contribution to the OM in the sediments, with values lower than 1 (Table 1) (Commendatore and Esteves, 2004).

Carbon preference index (CPI) values close to 1 indicates petrogenic hydrocarbons inputs to the sediments, while natural inputs

Table 1
Total organic carbon (TOC) and total nitrogen (TN) and parameters for sedimentary aliphatic hydrocarbons from sediments of Sergipe River estuarine system.

| Sample	TOC (%)	TOM (%)	C/N	Silt–Clay (%)	C_{max}	UCM (%)	∑n-alkane (µg g^{-1} dw)	UCM (µg g^{-1} dw)	RA (µg g^{-1} dw)	TAH (µg g^{-1} dw)	CPI	TAR	UCM/RA	UCM/n-alkane	LMW/HMW
P1	0.7	2.4	ND	8.9	C29	82.7	15.0	140.8	29.5	170.3	2.9	9.6	4.8	9.4	0.3
P2	2.4	11.1	15.6	22.3	C29	83.1	22.0	253.0	51.2	304.2	2.7	6.1	4.9	11.5	0.2
P3	0.3	1.4	ND	10.7	C29	60.7	11.2	50.8	32.9	83.7	2.8	4.2	1.5	4.5	0.4
P4	0.1	0.2	270.3	0.2	C15	ND	12.1	ND	12.5	12.5	1.1	1.6	ND	ND	0.4
P5	1.9	4.4	19.9	35.5	C15	ND	10.8	ND	18.4	18.4	1.2	9.1	ND	ND	0.4
P6	3.2	10.8	26.5	17.5	C29	77.0	30.8	228.3	68.3	296.6	3.9	10.8	3.3	7.4	0.3
P7	1.7	6.5	ND	21.7	C29	90.4	30.5	500.1	53.1	553.2	2.9	4.9	9.4	16.4	0.4
P8	0.2	1.0	ND	2.8	C29	81.9	19.8	178.5	39.3	217.8	2.6	1.9	4.5	9.0	0.7
P9	0.3	1.3	ND	8.1	C29	73.5	9.9	31.1	11.2	42.3	4.1	9.5	2.8	3.1	0.4

ND – not determined.
dw – dry weight.
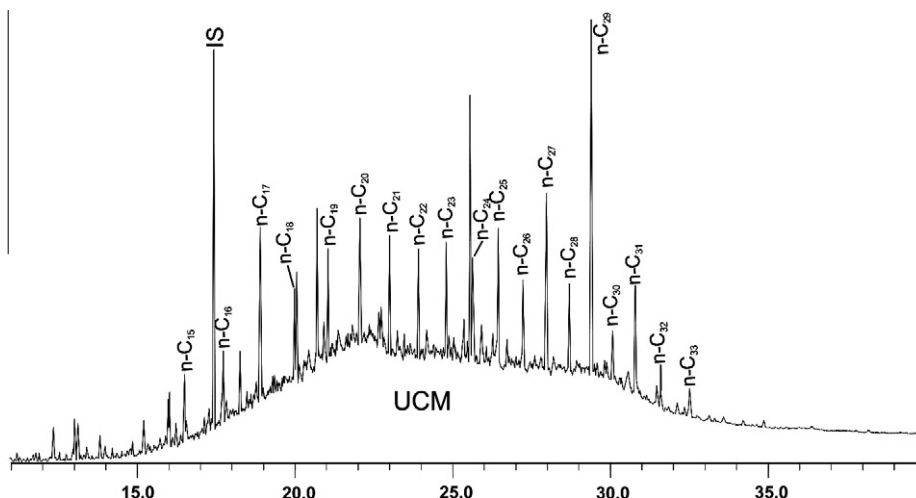
Fig. 2. GC-FID chromatogram of aliphatic hydrocarbons distribution and UCM from site P7.

have values higher than 3 (Commendatore and Esteves, 2004; Maioli et al., 2010b). Values close to 1 were only found in P4 and P5 sites, while all the others presented values close to or higher than 3, suggesting a mix of hydrocarbons sources to the sediments. These data also agree with the values found for nC_{max}, LMW/HMW and TAR indexes.

Along with linear aliphatic hydrocarbon, the amount of unresolved complex mixture (UCM) is of special interest for tracing anthropogenic contamination in marine ecosystems (Fig. 2). In the present study, UCM concentration values ranged from 31.1 μg g^{-1} at sampling site P9 up to 500.1 μg g^{-1} at site P7.

When eluting between nC_{16} and nC_{22}, UCM may be considered to be formed by bacterial degradation of natural organic inputs, such as algal detritus (Venkatesan and Kaplan, 1982; Oliveira and Madureira, 2010); conversely, UCM, upon its characteristics, may also suggest environmental contamination caused by petroleum, and its area in a gas chromatogram can be used to assess chronic pollution (Killops and Killops, 2005).

This work shows UCM eluting from nC_{14} up to nC_{34}. Despite of sites P4 and P5, where no UCM was found, the values reported are slightly higher when comparing to others studies (Tarozo et al., 2010; Asia et al., 2009; Hu et al., 2009). As may be inferred, these results are indicative of source mixture, including products of bacterial degradation and petroleum pollution.

The UCM abundance compared to the resolved alkanes (RA) may serve as diagnostic criterion of pollutant inputs. It also can be an estimate of organic matter degradation degree (Commendatore and Esteves, 2004; Maioli et al., 2010b). In this study, the range of UCM/RA ratio went from 1.5 at P3 site up to 9.4 at P7. According to Lipiatou and Saliot (1991) and Maioli et al. (2010b), UCM/RA values higher than 4 confirm the widespread presence of petroleum related residues. In our study, besides P7 site, all others have showed values in the range of 4 (P1, P2 and P8) or lower (P3, P4, P5, P6 and P9), suggesting mix input to the sediment or mild degradation processes.

No significant amounts of petroleum biomarkers, such as hopanes, were found in any of the analyzed sediments. The lack of these compounds may suggest non-petroleum input to the sediments or a highly degraded environment. Since the distribution of aliphatic hydrocarbons have suggested a mix source of OM to the sediments, it is reasonable to consider that the Sergipe River estuarine system may be influenced by the off shore petroleum exploration but the amount of it may not be a threat to the environment.

Conclusions

The hydrocarbons distribution in the superficial sediments of Sergipe River estuarine have permitted to assess the OM sources. Along with the levels of aliphatic hydrocarbons, the supplementary data of TOC and TN, as well as the CPI and TAR ratios have demonstrated that the data point to a mix of OM to the sediments. The UCM, found in all samples, except for sites P4 and P5, corroborates to our finds. At P7 site, on the other hand, it was observed that UMC/RA values suggest a minor petroleum contamination. In conclusion, despite its vulnerability, the Sergipe River estuarine system is not showing any important impact either from the petroleum exploration or the urban inputs. However, due the characteristics of this ecosystem, it is possible that any contamination input may be dilute with natural OM in the sediments, either from autochthones or allochtones sources.

Acknowledgments

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