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RESEARCH ARTICLE

Using stable isotopes to discriminate anthropogenic impacts of the sedimentary organic matter pollution in the Rodrigo de Freitas Lagoon (RJ, Brazil)

Mariana Vezzone[1,2] · Roberto Meigikos dos Anjos[2] · Ricardo Gonçalves Cesar[3] · Marcelo Muniz[2] · Renan Cardoso[2] · João Paulo Felizardo[2] · Daniela Vasconcelos[4] · Helena Polivanov[1]

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Abstract

Over the last decades, the Rodrigo de Freitas Lagoon (RFL), Rio de Janeiro, Brazil, has been impacted by the release of untreated domestic sewage, causing eutrophication processes with negative effects on its biota. Recently, the RFL underwent urban interventions to fulfill the demands of the 2016 Olympic Games, which included building the waist gallery and monitoring clandestine waste discharges into the underground drainage network. Organic-source tracing methods can be successfully used to characterize the organic matter transported from the urbanized areas to the RLF. The application of the elemental (C, N) and stable isotope (δ^{15}N and δ^{13}C) fingerprint methods in sediments from the RLF indicated a reduction in the domestic sewage inputs from 32 ± 16 to 12 ± 13% between 2015 and 2017. However, the sewage inputs continue being worrying. Our results also suggest that the main source of organic matter pollution in the lagoon comes from indiscriminate domestic sewage release from river channels. Secondary pollution sources are associated with the underground drainage network that still shows punctual and irregular releases of domestic sewage. Petroleum products, mainly from sewers, also show as possible organic pollution sources. Finally, the findings indicate that the interventions carried out in the RFL are promising. However, they were insufficient to cease the pollutant inputs and mitigate the negative impacts of eutrophication.

Keywords Untreated domestic sewage · Urban interventions · 2016 Olympic Games · Total stable isotopes of carbon and nitrogen

Highlights
• Previous actions have not resulted in significant effects on organic matter pollution
• Although the domestic sewage contribution has declined, it is still representative
• The main sewage sources are the drainage basins in the Rodrigo de Freitas Lagoon area

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✉ Mariana Vezzone
mvezzone@ufrj.br

[1] Departamento de Geologia, CCMN – Instituto de Geociências, Federal University of Rio de Janeiro, UFRJ, Av. Athos da Silveira Ramos, 274 – Cidade Universitária, Rio de Janeiro, RJ, Brazil

[2] Instituto de Física, Federal Fluminense University, UFF, Av. Litorânea, s/n - Praia Vermelha, Niterói, RJ, Brazil

[3] Departamento de Geografia, CCMN – Instituto de Geociências, Federal University of Rio de Janeiro, UFRJ, Av. Athos da Silveira Ramos, 274 – Cidade Universitária, Rio de Janeiro, RJ, Brazil

[4] Departamento de Geoquímica, Instituto de Química, Federal Fluminense University, UFF, Outeiro São João Batista S/N., Niterói, RJ, Brazil

Introduction

The urban expansion in coastal areas has intensified the contribution of domestic effluents without adequate wastewater treatment for the lagoon and fluvial ecosystems along South American coast, especially in the Brazilian coast (Carreira and De Wagener 1998; Abessa et al. 2005; Couceiro et al. 2007; Barros et al. 2010; Castro et al. 2016). The effluents, in addition to show high levels of organic matter (MO), usually have high concentrations of ammonia, sulfides, drugs, hormones, and toxic metals, among other contaminants of recognized toxicity, inducing the eutrophication of aquatic environments and severe damages to their biota (Huijbregts and Seppälaä 2001; Ansari et al. 2010; Quadra et al. 2017; Vezzone et al. 2019). Sediments and pollutants from soil erosion and leaching processes are also transported to water bodies, resulting in severe environmental impacts, such as silting of distribution channels and water reservoirs, contributing to the reduction of water quality and degradation habitats of terrestrial and aquatic ecosystems (Imeson 1995; Cardoso 2018). Eutrophication promotes the accumulation of organic carbon in the sediment and changes the accumulation balance of autotrophic and heterotrophic biomass in the sediment (Bucolo et al. 2008). These impacts may cause ecological effects, including macro and microalgae blooms (some species may be toxic) and, consequently, decreased dissolved oxygen and fish mortality (Caumette et al. 1996; Gao et al. 2012; Glibert 2017). Even subtle changes in coastal ecosystems can modify the food chains, resulting in variations on the isotopic composition of phytoplankton, zooplankton, and benthic communities, as well as populations of fish, crustaceans, and mollusks (Dudley and Shima 2010; Žvab Rožič et al. 2014; Oakes and Eyre 2015). This scenario is particularly critical in the coastal region of the State of Rio de Janeiro, where contamination by sanitary sewage and erosion processes severely affects the river and lagoon systems of Barra da Tijuca and Jacarepaguá, Rodrigo de Freitas Lagoon, Baixada Fluminense river channels, and lagoon systems of the Lagos region, among others (Carreira et al. 2002; Loureiro et al. 2009; Gonzalez et al. 2010; Monte et al. 2018).

The comprehensive characterization of the organic matter sources and their associated sediments in a catchment is necessary to understand and assess the impacts resulting from different land uses and effluent disposal (Carter et al. 2003; Reiffarth et al. 2016). The identification of the organic matter sources is therefore fundamental for the determination of pollutant sources and allocation of responsibilities in the waste management and recovery of environmental costs of water services, especially concerning the organic matter derived from the sewage waste discharge or agricultural activities. This information is essential for planning, management, and decision-making of land-use practices, sanitation, and preservation of aquatic biodiversity (Ansari et al. 2010; Owens et al. 2016; Quinn et al. 2017).

The natural sources of sedimentary organic matter may be of autochthonous origin, which comes from the primary production of the ecosystem itself, or allochthonous, derived from the fluvial discharge, continental drainage, and the ocean (Remeikaitė-Nikienė et al. 2016). The elemental (C, N) and stable isotope (δ^{15}N and δ^{13}C) fingerprint methods are often applied in lagoon sediments to determine the organic matter sources (Fry 2006; Gao et al. 2012; Mwaura et al. 2017). Fertilizers, animal waste, or domestic sewage are the main nitrate pollution sources in the hydrosphere (Hoefs 1997). In general, biotracers from bulk stable isotopes can be used as indicators of environmental changes and for the geochemical monitoring of impacted areas (Fry 2006; Ansari et al. 2010; Rumolo et al. 2011). Rumolo et al. (2011) confirmed that clusters analysis (CA) of δ^{13}C, δ^{15}N, C, and N values allows to discriminate the sedimentary organic matter of terrestrial origin, as well as to infer about the anthropogenic contribution. In particular, the authors demonstrated the high potential of δ^{15}N in discriminating sources of sewage discharges, indicating spatially the emission points.

The Rodrigo de Freitas Lagoon (RFL) is a typical urban lagoon in the Brazilian coast that is highly eutrophicated and contaminated by metal and organic matter pollutants (Stefens et al. 2007; Loureiro et al. 2009; da Fonseca et al. 2014; Vezzone et al. 2019). Given the 2016 Olympic Games, the monitoring of the water quality was intensified. Characterizations of the organic matter sources in the bottom sediments have become essential for the definition of the interventions that have been carried out in 2015. They also enabled an initial assessment of the effectiveness of the sewage treatment system and underground drainage network. This approach was pioneer in the studies carried out in the RFL over the last decades (Loureiro et al. 2009; Baptista Neto et al. 2011; Fonseca et al. 2011) and its execution can serve as a general model to be applied in other eutrophic urban lagoons along the Brazilian coast.

The present work aimed therefore to evaluate the environmental impacts before and after the 2016 Olympic Games, by identifying the organic matter sources in the RLF bottom sediments. Elemental (C and N) and stable isotope (δ^{13}C and δ^{15}N) analysis were carried out. The main working hypotheses are as follows: (i) domestic sewage contamination plays a major role in the pollution of bottom sediments; and (ii) the anthropic contribution of contamination after the Olympic Games is smaller compared with the previous period.

Materials and methods

Study area

The Rodrigo de Freitas Lagoon (RLF) is in the Southern zone of the Rio de Janeiro city (22° 57′ 02″ S, 43° 11′ 09″ W), with a total area of 2.2 km^2 and an average depth of 2.8 m (Fig. 1).

Its drainage area is about 24 km^2 (Soares et al. 2012) and is composed of Macacos (7.9 km^2), Cabeça (1.9 km^2), and Rainha (4.3 km^2) rivers sub-basin (Fig. 1), which are the main freshwater inputs to the RLF. The Cabeça and Macacos Rivers flow into the channel of General Garzon Street (M in Fig. 1). The Rainha River flows into the channel of Visconde de Albuquerque Street (CVA in Fig. 1). The channels of General Garzon Street and Visconde de Albuquerque Street are interconnected by the Jockey Club Channel (JC). There is a floodgate system that prevents the waters from the General Garzon Channel freely flow to the lagoon, as it can overflow during high flow periods (summer).

The geology of the watershed is predominantly of Precambrian gneiss rocks (facoidal gneiss, leptinite, kinzigite, and biotite gneiss) and subordinate quartzites, with intrusions of granite rocks. Granites and gneisses are intersected by basalt and diabase dikes. The slopes and low parts of the plain are composed of colluviums and talus of material from the erosion of the highest parts of the relief (Techno-Bio 2012).

The majority of the basin's land area is covered by the Atlantic Forest biome, composed of the Tijuca Rainforest (Soares et al. 2012). About a quarter of the basin is urbanized, including the districts of Ipanema, Leblon, Gávea, Jardim Botânico, Humaitá, and Lagoa that have the highest Human Development Index (HDI) in the city. On the other hand, the RFL also include the communities of Modesto Brocos, Rocinha, Parque da Cidade, and Chácara do Céu, where sanitary infrastructure is not adequate. Around the RFL, there are

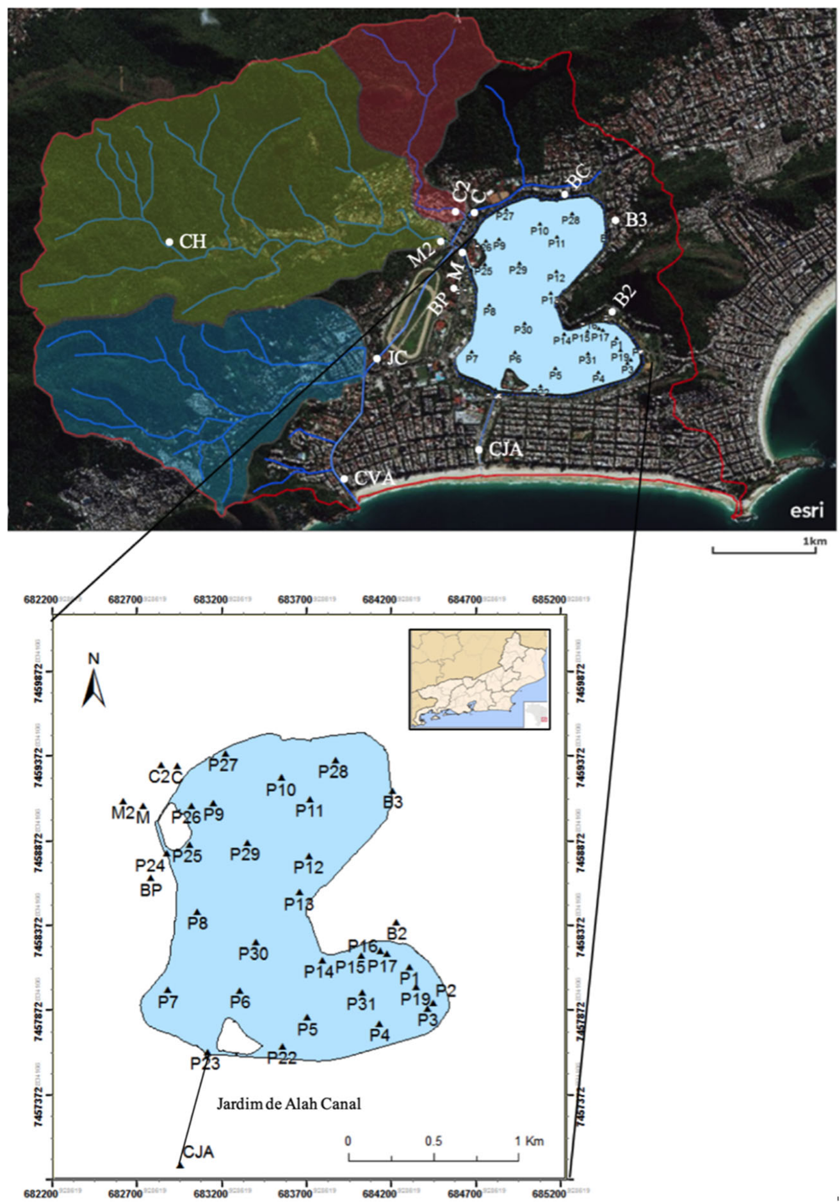


Fig. 1 Spatial location of the sediment sampling in the Rodrigo de Freitas Lagoon (P1–P16 in 2015 and P1–P31 in 2017) and in the drainage basin: CH, Horto Waterfall; M, Macacos River (General Garzon Street Channel); M2, Macacos River; CVA, Visconde de Albuquerque Street Channel; CJA, Jardim de Alah Channel; JC, Jockey Club Channel; C, Cabeça River; C2, Cabeça River 2; BC, control storm drain; BP, fuel station storm drain; B2, fuel station storm drain 2; B3, fuel station storm drain 3. Rainha River sub-basin in blue. Macacos River sub-basin in yellow. Cabeça River sub-basin in red. Modified from ESRI (2016)

about 24 points of the rainwater system contaminated by illegal sewage dumping into its underground drainage network (Loureiro et al. 2009; Vezzone et al. 2019).

The RFL is a semi-confined system where water renewal is complex and the marine water flux is superficial, leaving deeper layers unaffected (Torres 1990; da Fonseca et al. 2014). The lagoon has a single connection with the sea (Jardim de Alah Canal, a mechanical locking system), located near the artificial island in the southern part of the Lagoon. Previous studies reported high metal concentrations (Loureiro et al. 2009; Vezzone et al. 2019), fecal contamination (Gonzalez et al. 2010; da Fonseca et al. 2014), eutrophication, chemical contamination (Stefens et al. 2007; Soares et al. 2012), and events of massive fish death overtime (Domingos et al. 2012).

Sampling

Sediment sampling from the surface layers of the lagoon bottom was carried out in the dry seasons of June 2015 and August 2017, by using a Van Veen grab 250-cm^2 sampler (KC Denmark A/C, Denmark). Sediment samples were georeferenced, using a GPS device (Garmin Ltd., model eTrex 30X, São Paulo, Brazil). In 2015, bottom sediments (up to 10 cm depth) was collected at 16 points (P1 to P16 in Fig. 1). In 2017, bottom sediments (up to 2.0 cm depth) were collected. The bottom layer thickness of 2.0 cm depth was estimated from the sedimentation rate of 0.75 cm/year previously proposed by Loureiro et al. (2009). It was chosen to avoid the influence of sediments that would have been deposited before the construction of a new sanitary sewer system for the 2016 Olympic Games. Bottom sediment samples were collected at 29 points: P1 to P17, P19, P22 to P31 in Fig. 1, with P1–P16 corresponding to the same locations as the sampling carried out in 2015. P17, P19, and P22 to 28 are located close to rainwater outlets, corresponding, therefore, to the main sediment accumulation sites. P29, P30, and P31, in turn, are in the central part of the RFL. In the 2017 fieldwork, bottom sediments were also sampled at the strategic points of the river sub-basins to evaluate the persistent organic pollutant features that join the RFL. The strategic points were Cabeça River (C, C2), Macacos River (M2), Horto Waterfall (CH), Jockey Club Channel (JC), Visconde de Albuquerque Street Channel (CVA), General Garzon Street Channel (Macacos River after junction with Rio Cabeça and Jockey Channel Club = M), Jardim de Alah Canal (CJA), and storm drains around the lagoon (BP, BC, B2, and B3).

The samples were stored into Ziplock bags and transported under refrigeration to the laboratory. They were kept at − 8 °C in a freezer until analysis.

Grain size and pH analysis

At the laboratory, sediment samples (400–500 g) were dried in an oven at 40 °C for 24 h to obtain their dry mass values. Subsequently, they were homogenized and subdivided according to the amount necessary for the physical and chemical analysis.

Grain size analysis was performed by wet sieving method (EMBRAPA 1997), where the organic matter was removed by adding 30% H_2O_2. A dispersing agent, Calgon (35.7 g of sodium hexametaphosphate and 7.94 g of sodium carbonate in 1.0 L of distilled water), was added to 50 g of the sample, and the wet mixture was passed through a 63-µm sieve. The retained material was dried and evaluated as sand fraction (> 63 µm). The material that passed through the sieve (< 63 µm) was stored in a 1-l graduated cylinder, such that the silt (63 to 4 µm) and clay (< 4 µm) fractions were separated through the difference in their settling rates.

The pH values were determined in the laboratory by weighing 10 g of dried sample and adding 25 ml of ultrapure water (EMBRAPA 1997). After being mixed for 1 h, the pH values were determined using a combined electrode with a benchtop pH-meter (model Q400a, Quimis, Brazil).

Elemental and stable isotope analysis

Values of total organic carbon (TOC), total nitrogen (TN), and stable isotope ratios of organic carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) were determined in the Radioecology Laboratory and Environmental Changes (LARA) of the Federal Fluminense University (UFF). For organic carbon measurements (TOC and $\delta^{13}C_{org}$), the sediment samples were initially subjected to a decarbonization process to avoid interference of inorganic carbon (Gibbs 2014) by acid washing with HCl (1 M), followed by ultrapure water washing. Subsequently, they were dried at 40 °C and about 0.20 mg per sample were introduced into tin capsules. For nitrogen analysis (TN and $\delta^{15}N$), samples were desalinated and dried at 40 °C for 24 h. About 0.40 mg per sample were stored into tin capsules.

Values of $\delta^{13}C_{org}$ and $\delta^{15}N$ were determined by using an elemental analyzer coupled to an isotope ratio mass spectrometer (EA-IRMS). The LARA system consists of a FlashEA2000 elemental analyzer interfaced to a DELTA V Advantage Isotope Ratio Mass Spectrometer (Thermo Electron Corp., Bremen, Germany). The bulk samples were initially combusted at 1020 °C in the EA reactor under continuous helium flow. The gas passes through two reactors to eliminate contaminating gases, such as sulfur (S) and water (H_2O) residues, and the resulting CO_2 and N_2 gases are injected into the IRMS, which allows determining the values of $\delta^{13}C$ and $\delta^{15}N$. The analytical error measured between the replicates of the standard sample was at most ± 0.2‰ and ± 0.3‰, respectively. Samples were analyzed together with empty tin capsules (blank) and reference materials: IVA33802174 urea ($\delta^{13}C = -41.3 \pm 0.04$, $\delta^{15}N = -0.32 \pm 0.02$), IAEA-600 caffeine ($\delta^{13}C = -27.771 \pm 0.043$; $\delta^{15}N = 1.0 \pm 0.2$), Elemental Microanalysis soil ($\delta^{13}C = -26.66 \pm 0.24$; $\delta^{15}N = 7.30 \pm 0.13$), and USGS24 graphite ($\delta^{13}C = -16.049 \pm 0.035$).

Statistical analysis

Statistical analysis was performed using R software version 3.5.1 (R Core Team 2018). The data obtained from 2015 and 2017 were compared by Kruskal-Wallis test of variance since the Shapiro-Wilk normality test was not observed in all cases.

Results

Particle size and pH

According to Fig. 2a and b, it is possible to evaluate the changes in the accumulation rate between the mud (silt + clay) and sand fractions during 2015 and 2017, respectively. One can observe that although the mud accumulation remains predominant (> 50%) in more than two-thirds of the lagoon, there was a decrease in the southern part in 2017.

Although the pH values in bottom sediments ranged between 3.8 and 7.6, showing more acidic values in the northern part (Table 1), on average, there were no significant changes between 2015 ($\overline{\text{pH}}$ = 5.5) and 2017 ($\overline{\text{pH}}$ = 6.0); Kruskal-Wallis, p value > 0.05.

TOC, NT, and atomic TOC/TN

The values of TOC, TN, and atomic TOC/TN from bottom sediment sampling in 2015 and 2017 are reported in Table 1. TOC ranged from 0.3 to 6.7% (n = 16, mean = 3.8 ± 1.7%) in 2015, and 0.6 to 13.7% (n = 29, mean = 5.3 ± 3.2%) in 2017. TN ranged between 0.04 and 0.5% (n = 16, mean = 0.3 ± 0.1) in 2015, and 0.05% and 1.45% (n = 29, mean = 0.60 ± 0.4%) in 2017. Low values of TOC (Fig. 2c and d) and TN (Fig. 2e and f) were observed in the southern part of the lagoon. However, it is possible to note that there was a reduction in the values of TOC and TN between 2015 (Fig. 2c and e, respectively) and 2017 (Fig. 2d and f, respectively). The values of atomic TOC/TN ranged from 7.0 to 15.6 (n = 16, mean = 12.5 ± 2.3) in 2015, and 5.0 to 42.0 (n = 29, mean = 12.9 ± 7.7) in 2017. From Fig. 2g (2015) and h (2017), there was a significant reduction in the atomic TOC/TN values in 2017 (Kruskal-Wallis, p value < 0.05). However, there was an increase around the P23 (Visconde de Albuquerque Street Channel in Fig. 1) in 2017.

The sediment samples from the drainage basin collected in 2017 (C, C2, M2, CH, JC, CVA, M, CJA, BP, BC, B2, and B3 in Table 1 and Fig. 1) showed values of TOC ranging between 0.04 and 10.4% (n = 11, mean = 2.7 ± 3.5%) and TN values between 0.01 and 0.5% (n = 11, mean = 0.2 ± 0.1%). The lowest TOC value (i.e., below the detection limit) were found in CJA (Jardim de Alah Canal). Values of atomic TOC/TN are ranging between 8.2 and 60.7, being 73% of them (n = 11) with values above 15.

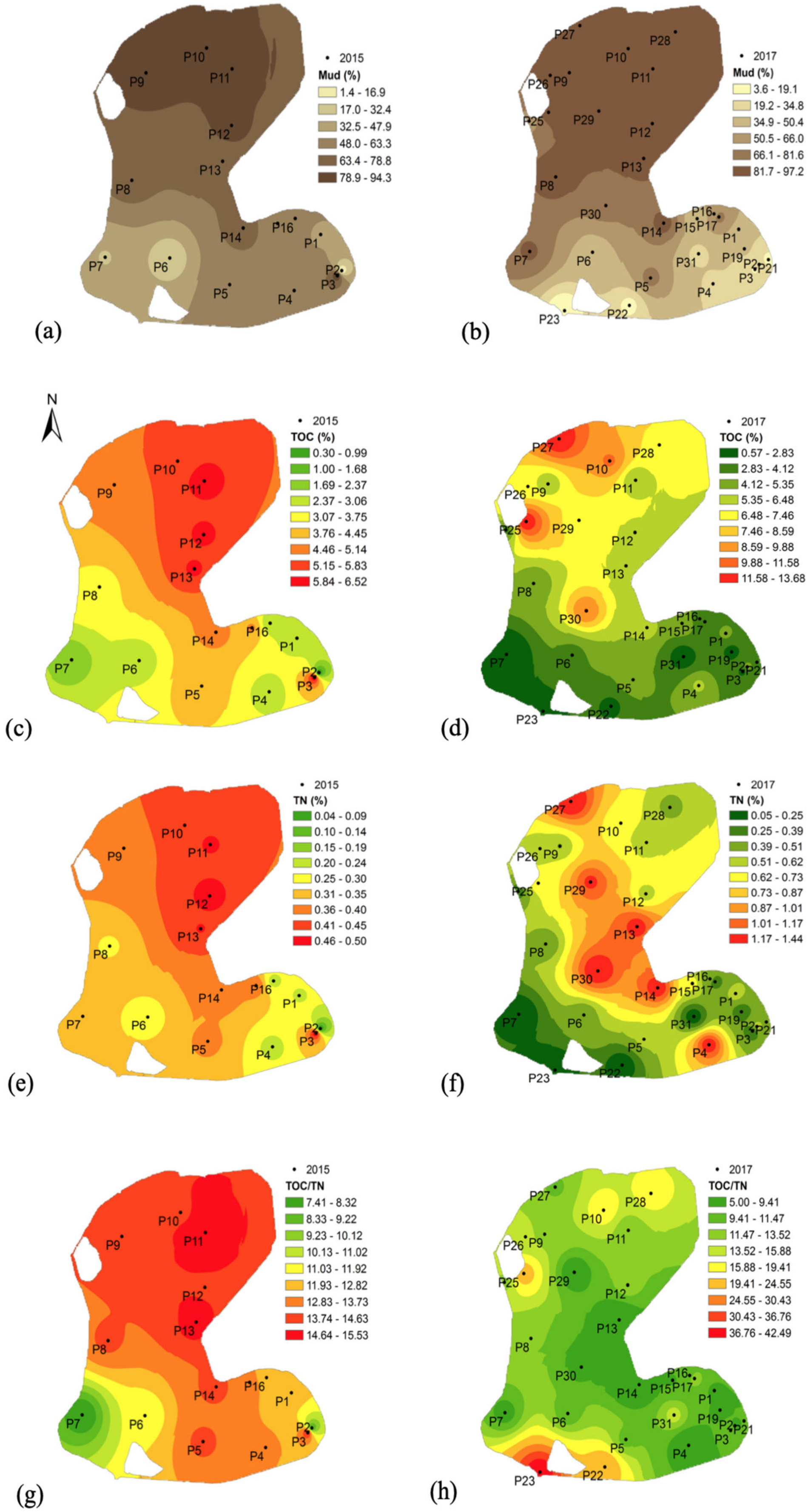
$\delta^{13}C_{org}$ and $\delta^{15}N$

Table 1 and Fig. 3 show that, in 2015, $\delta^{13}C_{org}$ in bulk bottom sediments ranged from − 24.4 to − 22.1‰ (n = 16, mean = − 23.4 ± 0.7‰) and from − 26.9 to − 21.5‰ (n = 29, mean = − 24.1 ± 1.1‰) in 2017. The most enriched values were found in the RFL southern sector (P1, P4, P8, and P16 in Fig. 3a) in 2015, and P16, P17, and P22 (Fig. 3b) in 2017. In turn, $\delta^{15}N$ presented values between 4.7 and 6.5‰ (n = 16, mean = 5.8 ± 0.5‰) in 2015 (Fig. 3c), and 4.6 and 7.7‰ (n = 29, mean = 6.6 ± 0.7‰) in 2017 (Fig. 3d). In the drainage basin, $\delta^{13}C_{org}$ and $\delta^{15}N$ ranged from − 28.9 to − 21.6‰ (n = 11, mean = − 26.1 ± 2.1‰) and 1.4 to 7.3‰ (n = 11, mean = 4.3 ± 1.8‰), respectively (Table 1).

Discussion

The grain size distribution significantly influences the geochemical behavior of the elements in the sediments (Förstner and Wittmann 1981). The understanding of the RLF hydrodynamics is closely correlated with the gran size distribution of its sediments. Sediment in wave-dominated estuaries, such as RFL, generally ranges from fine to coarse sands in the barrier, fine organic muds and sandy muds in the central part of the lagoon, to coarse sands and muds in the fluvial delta, mainly of terrigenous origin (Nichol 1991). The RLF has a single connection to the sea, located in the southern part of the Lagoon (Jardim de Alah Channel - CJA, next to P23 in Fig. 1). CJA is a protective barrier that has a constricted entrance (which can be periodically closed) that allows the exchange of water between the lagoon and the sea. Therefore, CJA limits the wave penetration while transports water and sandy marine sediments into the lagoon (Vezzone et al. 2019). Therefore, if the CJA is working properly, the marine water inputs will contribute to increase the hydrodynamics and dissolved oxygen in the lagoon, resulting in the fine-particle resuspension with alterations in the TOC values and oxidation of organic matter, respectively (Vezzone et al. 2019). On the other hand, if there is a poor exchange with the marine environment, such as silting up or an intermittent or non-existent opening of the CJA's mechanical locking system, the RFL can act as an efficient trap for terrigenous sediment and pollutants.

According to the particle size (Fig. 2a and b) and TOC (Fig. 2c and d) results, sediments with high sandy and low organic matter contents, respectively, are observed in the CJA vicinity. In the northern part, on the other hand, the sewage-contaminated river inputs and the low hydrodynamics contribute to the increase of the mud and organic matter contents (Soares et al. 2012; Vezzone et al. 2019). Comparing the


• 2015
Mud (%)
1.4 - 16.9
17.0 - 32.4
32.5 - 47.9
48.0 - 63.3
63.4 - 78.8
78.9 - 94.3
P10 P9 P11 P12 P13 P8 P14 P16 P1 P7 P6 P2 P3 P5 P4
(a)
• 2017
Mud (%)
3.6 - 19.1
19.2 - 34.8
34.9 - 50.4
50.5 - 66.0
66.1 - 81.6
81.7 - 97.2
P27 P28 P10 P26 P9 P11 P25 P29 P12 P13 P8 P30 P16 P14 P15 P17 P1 P7 P6 P31 P19 P2 P21 P3 P5 P4 P23 P22
(b)
N
• 2015
TOC (%)
0.30 - 0.99
1.00 - 1.68
1.69 - 2.37
2.37 - 3.06
3.07 - 3.75
3.76 - 4.45
4.46 - 5.14
5.15 - 5.83
5.84 - 6.52
P10 P9 P11 P12 P13 P8 P14 P16 P1 P7 P6 P2 P3 P5 P4
(c)
• 2017
TOC (%)
0.57 - 2.83
2.83 - 4.12
4.12 - 5.35
5.35 - 6.48
6.48 - 7.46
7.46 - 8.59
8.59 - 9.88
9.88 - 11.58
11.58 - 13.68
P27 P28 P10 P26 P9 P11 P25 P29 P12 P13 P8 P30 P16 P14 P15 P17 P1 P7 P6 P31 P19 P2 P21 P3 P5 P4 P23 P22
(d)
• 2015
TN (%)
0.04 - 0.09
0.10 - 0.14
0.15 - 0.19
0.20 - 0.24
0.25 - 0.30
0.31 - 0.35
0.36 - 0.40
0.41 - 0.45
0.46 - 0.50
P10 P9 P11 P12 P13 P8 P14 P16 P1 P7 P6 P2 P3 P5 P4
(e)
• 2017
TN (%)
0.05 - 0.25
0.25 - 0.39
0.39 - 0.51
0.51 - 0.62
0.62 - 0.73
0.73 - 0.87
0.87 - 1.01
1.01 - 1.17
1.17 - 1.44
P27 P28 P10 P26 P9 P11 P25 P29 P12 P13 P8 P30 P16 P14 P15 P17 P1 P7 P6 P31 P19 P2 P21 P3 P5 P4 P23 P22
(f)
• 2015
TOC/TN
7.41 - 8.32
8.33 - 9.22
9.23 - 10.12
10.13 - 11.02
11.03 - 11.92
11.93 - 12.82
12.83 - 13.73
13.74 - 14.63
14.64 - 15.53
P10 P9 P11 P12 P13 P8 P14 P16 P1 P7 P6 P2 P3 P5 P4
(g)
• 2017
TOC/TN
5.00 - 9.41
9.41 - 11.47
11.47 - 13.52
13.52 - 15.88
15.88 - 19.41
19.41 - 24.55
24.55 - 30.43
30.43 - 36.76
36.76 - 42.49
P27 P28 P10 P26 P9 P11 P25 P29 P12 P13 P8 P30 P16 P14 P15 P17 P1 P7 P6 P31 P19 P2 P21 P3 P5 P4 P23 P22
(h)

◀ **Fig. 2** Spatial distributions of (**a**) mud (%) in 2015, (**b**) mud (%) in 2017, (**c**) TOC (%) in 2015, (**d**) TOC (%) in 2017, (**e**) TN (%) in 2015, (**f**) TN (%) in 2017, (**g**) TOC/TN in 2015, and (**h**) TOC/TN in 2017 in bulk bottom sediments from the Rodrigo de Freitas Lagoon

values of particle size and TOC obtained in 2015 and 2017, it is possible to observe that after the RFL revitalization works for the 2016 Olympic Games, there was an increase of the sand-sized sediment budget and a decrease in the organic matter contents in the southern part of the lagoon, suggesting a significant improvement in the exchange of water between the lagoon and the sea. In 2015, the findings about TOC (Fig. 2c) suggest a low water oxygenation in the northern sector since the water circulation was more restricted and favored the organic matter accumulation. This issue improved in 2017. However, it is possible to observe a few sites with high TOC values (around the Cabeça River mouth, P27 in Fig. 2d), suggesting that irregular sewage releases in the northern part of the lagoon are still occurring.

The more acidic pH values found for the northern sector are possibly due to the increase of organic matter contents (DeBusk 1988). Such observation, which is typical of reducing and eutrophic environments, is supported by the potential occurrence of high contents of sulfide minerals, ammonia in sediments, and anomalous concentrations of dissolved CO_2 in water column (Smith and Klug 1981), inducing acidic conditions, and the abundance of organic acids (Carrie et al. 1998), which can also contribute to the decrease of pH levels.

From the boxplot showed in Fig. 4, one can evaluate the empirical distribution of the TOC, TN, $\delta^{13}C_{org}$, and $\delta^{15}N$ from bottom sediment sampling in 2015 and 2017. Figure 4 a and b indicate that the values of TOC and $\delta^{13}C_{org}$ did not show significant changes between 2015 and 2017. Similar finding is obtained from the Kruskal-Wallis test (p value > 0.05). On the other hand, TN and $\delta^{15}N$ show an upward trend over time (Fig. 4c and d; Kruskal-Wallis, p value < 0.05), suggesting a decrease in sanitary sewage releases in the RFL between 2015 and 2017. Table 2 shows that typical values of $\delta^{15}N \sim 2.5‰$ are observed in untreated sewage, and organic matter of marine origin is ~ 9‰. These results are in accordance with the observations obtained from the particle size and TOC analyzes (Fig.2).

According to the observations from Rumolo et al. (2011) and results found from Fig. 2g and h for atomic TOC/TN values, it is possible to suggest that 31% of the bottom sediment samples in the RFL were predominantly marine origin in 2015, since the atomic TOC/TN values ranged between 4 and 12. In 2017, the marine sediment content increased to 55%. Considering the bottom samples that could clearly be characterized as being of terrestrial origin, showing value of atomic TOC/TN > 15 (Meyers 1997), Table 1 highlights that 25% of them collected in 2015 were within this range, decreasing to 20% in 2017. Additionally, the low correlation observed between TOC and TN (Fig. 5) suggests that nitrogen may be potentially related to anthropic sources with unbalanced TOC/TN values (Rumolo et al. 2011).

The most enriched $\delta^{13}C_{org}$ values were observed in the southern sector of the RFL (P1, P4, P7, P8, and P16 in Fig. 3a) in 2015. However, they were distributed in two main groups (with colors ranging from red to yellow), one on the left (around P7 and P8) and another on the right (around P1, P4, and P16) of the lagoon. In 2017, there was a great expansion of these groups, connecting and reaching the northern sector of the lagoon (Fig. 3b). According to Carreira et al. (2002), values of $\delta^{13}C_{org}$ around − 20‰ suggest that there is a higher contribution of marine organic matter. These results confirm the evidence observed from the distributions of particle size, TOC, and atomic TOC/N that show that there was a better marine water circulation into the lagoon after frequent dredging operations in the CJA and carrying out repair works on the CJA gates.

For sediment samples from rivers and channels (M, M2, C, C2, JC, VA, BC, BP, B2, B3, and CH in Table 1), the $\delta^{13}C_{org}$ values are shown to be more depleted ($n = 11$, mean = − 26.8 ± 1.4‰) than those found in the lagoon sediments ($n = 29$, mean = − 24.1 ± 1.1‰). As expected, these results indicate a high influence of the terrestrial organic matter in the drainage basin. The most depleted value of − 28.9‰ occurred around the CH (Horto Waterfall). Its sampling site is located around the environmental protected area of the Tijuca Rainforest that is supposedly free from anthropogenic sources. This result agrees with organic matter sources from plants C3, which have an average value of $\delta^{13}C_{org} = -28‰$ (Table 2).

According to Sweeney et al. (1980) and Morrissey et al. (2013), sites that show untreated sanitary sewage releases have typical values of $\delta^{15}N$ ranging between 0 and 5‰. The most depleted values were observed in the southern part of RLF (green colors around P8 and P16 in Fig. 3c) in 2015. In 2017, there was an expansion of the most depleted area on the western side of the lagoon (around P7, P8, P24, and 25 in Fig. 3d), while the southeastern side remained almost unchanged. This result suggests that even after the RFL revitalization works, there may still be a significant clandestine waste discharges into the underground drainage network in the RLF.

In the drainage basin, $\delta^{15}N$ average value was 4.3 ± 1.9‰, while for the lagoon sediments was 6.6 ± 0.7‰. More depleted $\delta^{15}N$ values can also be relative to C3 plants (Table 2). Therefore, it is important to assess the correlations between $\delta^{15}N$, $\delta^{12}C_{org}$, and TOC/TN to better discriminate the organic matter sources (Meyers 1994; Usui et al. 2006; Gao et al. 2012; Ke et al. 2017).

Distributions of TOC/TN × $\delta^{13}C_{org}$ and $\delta^{15}N \times \delta^{13}C_{org}$ are shown in Fig. 6. Values of $\delta^{13}C_{org}$ and $\delta^{15}N$ observed in previous studies (Table 2) were used as references of the organic matter sources from marine and terrestrial plants,

Table 1 Values of TOC, TN, TOC/TN, $\delta^{13}C_{org}$, and $\delta^{15}N$ in the bottom sediment samples from the Rodrigo de Freitas Lagoon (P1–P16 in 2015 and P1–P31 in 2017), and in water bodies (CJA; M; M2; C; C2; CVA; JC; CH in 2017) and storm drains (BC; BP; B2; B3 in 2017) in RFL drainage basin. *ND* data not available. *Average, min, and max values were calculated for the RFL sediment samples (P1–P31)

Sample	TOC (%)		TN (%)		TOC/TN (atomic)		$\delta^{13}C_{org}$		$\delta^{15}N$		pH	
	2015	2017	2015	2017	2015	2017	2015	2017	2015	2017	2015	2017
P1	2.6	4.4	0.2	0.6	15.2	8.6	−22.4	−23.4	5.4	6.5	7.0	6.9
P2	0.3	4.5	0.04	0.6	8.8	8.8	−24.0	−23.4	6.5	6.9	7.3	7.0
P3	6.7	2.5	0.5	0.3	15.6	9.7	−24.4	−23.1	6.3	6.7	6.9	7.6
P4	2.6	5.6	0.2	1.3	15.2	5.0	−22.1	−23.1	6.1	7.1	7.2	7.2
P5	4.5	4.9	0.4	0.5	13.1	11.4	−23.9	−24.3	6.1	7.0	4.4	5.3
P6	3.0	3.7	0.3	0.4	11.7	10.8	−24.1	−24.0	5.9	6.4	5.9	7.0
P7	1.8	0.6	0.3	0.1	7.0	7.0	−22.9	−24.1	5.6	5.7	6.3	6.0
P8	2.9	4.2	0.3	0.4	11.3	12.3	−22.4	−23.0	5.1	5.8	6.2	5.2
P9	4.4	5.5	0.4	0.5	12.8	12.8	−23.4	−24.8	6.5	6.8	3.8	6.2
P10	5.2	10.2	0.4	0.6	15.2	19.8	−23.9	−24.4	6.4	6.4	3.8	5.0
P11	5.4	5.4	0.5	0.5	12.6	12.6	−23.7	−24.0	5.3	7.3	4.0	4.0
P12	5.4	6.2	0.5	0.6	12.6	12.1	−23.9	−24.4	6.3	7.0	4.3	4.8
P13	5.6	6.0	0.5	1.3	13.1	5.4	−24.2	−24.3	5.9	7.4	4.2	5.3
P14	4.4	5.9	0.4	1.3	12.8	5.3	−23.6	−23.8	5.6	6.8	4.9	4.2
P15	3.8	5.2	0.4	0.7	11.1	8.7	−23.4	−23.3	5.8	6.8	5.8	7.4
P16	2.1	3.9	0.2	0.5	12.3	9.1	−22.4	−22.9	4.7	5.9	6.2	6.7
P17	ND	3.4	ND	0.3	ND	13.2	ND	−21.5	ND	6.1	ND	6.7
P19	ND	2.3	ND	0.3	ND	8.9	ND	−24.0	ND	5.8	ND	6.0
P21	ND	1.8	ND	0.2	ND	10.5	ND	−25.1	ND	5.2	ND	6.0
P22	ND	2.5	ND	0.1	ND	29.2	ND	−22.6	ND	7.7	ND	6.5
P23	ND	1.8	ND	0.05	ND	42.0	ND	−25.0	ND	6.5	ND	7.0
P24	ND	3.7	ND	0.3	ND	14.4	ND	−25.3	ND	4.6	ND	5.2
P25	ND	13.5	ND	0.7	ND	22.5	ND	−26.1	ND	6.2	ND	7.4
P26	ND	6.6	ND	0.6	ND	12.8	ND	−24.6	ND	6.5	ND	7.0
P27	ND	13.7	ND	1.4	ND	11.4	ND	−24.2	ND	7.0	ND	6.9
P28	ND	7.1	ND	0.5	ND	16.6	ND	−26.9	ND	6.4	ND	5.0
P29	ND	6.9	ND	1.2	ND	6.7	ND	−24.2	ND	7.2	ND	3.9
P30	ND	9.9	ND	1.4	ND	8.3	ND	−25.0	ND	7.1	ND	6.1
P31	ND	1.5	ND	0.1	ND	17.5	ND	−23.3	ND	7.6	ND	5.9
CJA	ND	0.04	ND	ND	ND	ND	ND	−21.6	ND	ND	ND	7.9
M	ND	0.2	ND	0.02	ND	11.7	ND	−27.1	ND	4.5	ND	6.3
M2	ND	0.3	ND	0.01	ND	35.0	ND	−24.1	ND	1.4	ND	6.4
C	ND	10.4	ND	0.2	ND	60.7	ND	−26.1	ND	5.2	ND	4.5
C2	ND	3.3	ND	0.2	ND	19.3	ND	−28.9	ND	3.5	ND	4.1
JC	ND	7.4	ND	0.2	ND	43.2	ND	−26.2	ND	3.3	ND	4.6
VA	ND	0.4	ND	0.02	ND	23.3	ND	−27.1	ND	2.3	ND	6.7
BC	ND	7.3	ND	0.5	ND	17.0	ND	−26.1	ND	5.4	ND	6.1
BP	ND	3.0	ND	0.2	ND	17.5	ND	−27.5	ND	5.2	ND	5.9
B2	ND	1.4	ND	0.2	ND	8.2	ND	−26.3	ND	6.5	ND	6.0
B3	ND	0.7	ND	0.05	ND	16.3	ND	−26.0	ND	7.3	ND	7.4
CH	ND	0.1	ND	0.01	ND	11.7	ND	−28.9	ND	2.4	ND	6.1
* Average ± σ	3.8 ± 1.7	5.3 ± 3.2	0.3 ± 0.1	0.6 ± 0.4	12.5 ± 2.3	12.9 ± 7.7	−23.4 ± 0.7	−24.1 ± 1.1	5.8 ± 0.5	6.6 ± 0.7	5.5 ± 1.3	6.0 ± 1.1
* Min	0.3	0.6	0.04	0.05	7.0	5.0	−24.4	−26.9	4.7	4.6	3.8	3.9
* Max	6.7	13.7	0.5	1.4	15.6	42.0	−22.1	−21.5	6.5	7.7	7.3	7.6

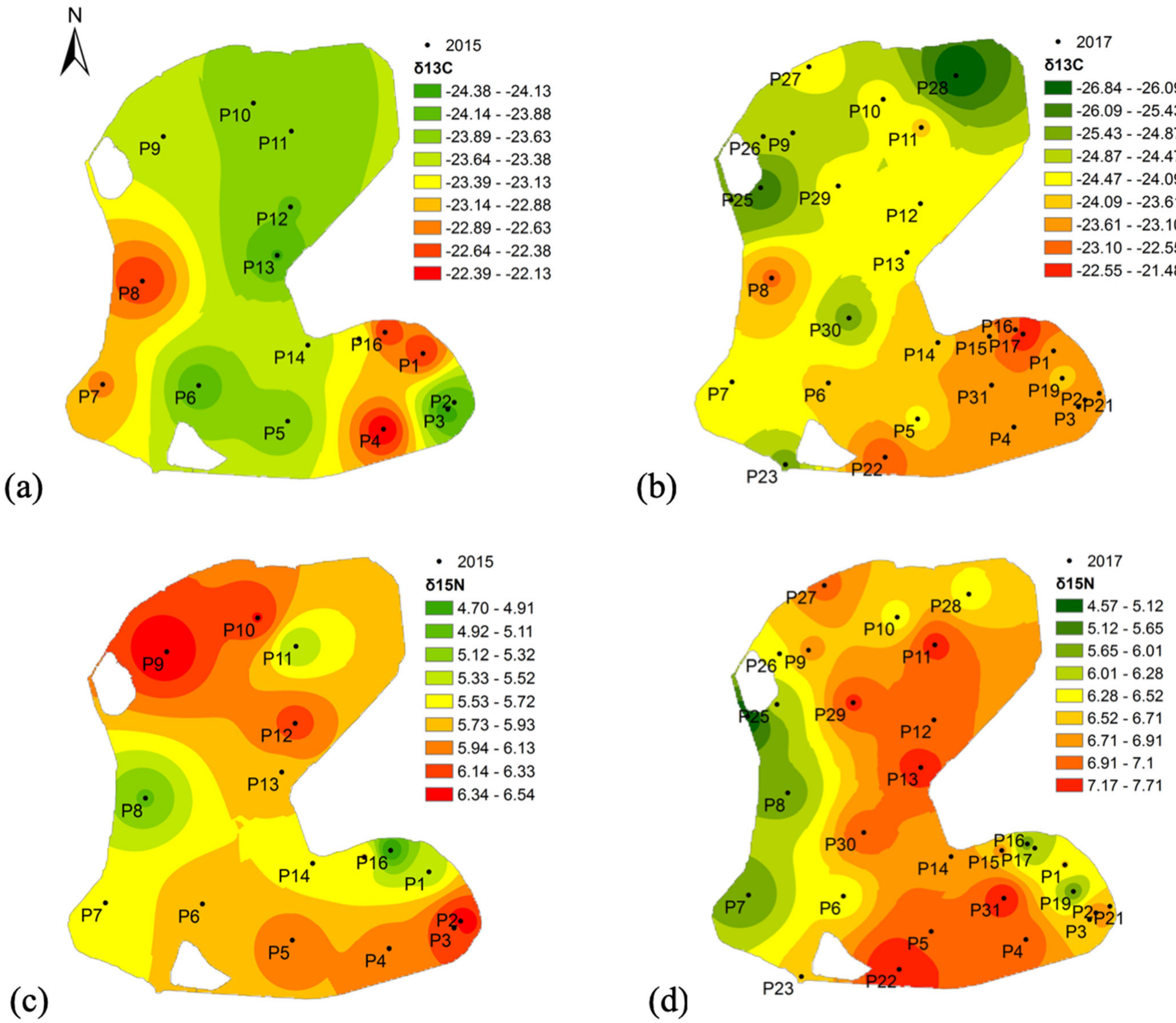


Fig. 3 Spatial distributions of (**a**) $\delta^{13}C_{org}$ in 2015, (**b**) $\delta^{13}C_{org}$ in 2017, (**c**) $\delta^{15}N$ in 2015, and (**d**) $\delta^{15}N$ in 2017 in bulk bottom sediments from the Rodrigo de Freitas Lagoon

sewage, and petroleum products. For TOC/TN, values ranging 4 to 12 were used to characterize marine organic matter sources (Rumolo et al. 2011). TOC/TN is > 15 for terrestrial sources (Meyers 1994) and between 7 and 10.5 for untreated sewage sources (Barros et al. 2010). From Fig. 6a, it is possible to observe that sediment samples from CH (Horto Waterfall) and C2 (Cabeça River 2) have predominantly terrestrial origin. This finding is consistent with their local features, since the drainage area of the Cabeça River is composed almost entirely by native forests and a small urban area (Fig. 1). In addition, the urban area has complete sanitary infrastructure with one of the largest HDI in the city (PNUD 2013). The most of the bottom sediment samples from the RFL (2015 and 2017) are concentrated around the cluster related to the untreated sewage releases. However, it is not possible to state that these samples are preferably characterized by the influence of sewage, since they have intermediate values that also suggest a mixture of marine and terrestrial sources. Still analyzing Fig. 6a, one could infer that the P25 and P28 (northern part of the lagoon) show more considerable terrestrial influence and the P22 (in the southern sector) have more significant marine influence. The P17 is more towards marine influence and in Fig. 6b is more towards sewage, suggesting that both sources could be significant for this bottom sediment sample.

From Fig. 6b, it is possible to triangulate the main sources and distinguishing more clearly the potential sources of organic matter since the isotopic composition is more sensitive to the influences of the sources. Most of the points are arranged between the possible sources (marine, terrestrial, sewage, petroleum products), suggesting that these are the primary sources of organic matter present in the RFL and its drainage

Table 2 Values of the bulk carbon and nitrogen isotopic ratios for organic matter sources

Source	$\delta^{13}C_{org}$ (‰)	$\delta^{15}N$ (‰)	Reference
Untreated sewage	− 24.4		(Carreira and De Wagener 1998)
	− 23.16 ± 0.4	1.50 ± 0.45	(Prado et al. 2020)
	− 23 ± 2.5		(Ramírez-Álvarez et al. 2007)
	− 22 to − 28.5		(Lee et al. 2020)
		2–3	(Sweeney et al. 1980)
	− 26.5 ± 0.1	2.3 ± 0.3	(Rogers 2003)
	− 22.8 ± 0.3	3.4 ± 0.2	(Roth et al. 2016)
		0–5	(Morrissey et al. 2013)
Marine	− 20		(Carreira et al. 2002)
	− 20 to − 22		(Meyers 1994)
	− 21.3 ± 1.1	8.6 ± 1	(Peterson et al. 1985)
	− 18 to − 22		(Lee et al. 2020)
	− 20.1 ± 0.1	6.5 ± 0.3	(Rogers 2003)
		8–12	(Barros et al. 2010)
	− 18 to − 22	4–10	(Lu et al. 2020)
		7–10	(Meyers 2003)
Terrestrial	− 26.5 – − 30.5	3–7	(Barros et al. 2010)
		1–13.8	(Rumolo et al. 2011)
		− 10 to 10	(Lu et al. 2020)
Plants C3	− 21 to − 35		(Meyers 1997)
	− 28.6 ± 1.3	− 0.6–1.3	(Peterson et al. 1985)
	~ − 28		(Guiry 2019)
		0.5	(Meyers 2003)
Petroleum Products	− 27 to − 30		(Widory 2006)
		> 9	(Rumolo et al. 2011)
	− 26.5 to − 27.1		(Yu et al. 2010)

basin. Although it is not possible to detail the direct influence of each source, evaluating the sources with more or less influence is feasible. The petroleum product source was included in order to assess the potential of this approach to distinguish possible fuel leaks from gas stations located around the lagoon. Even though this source did not seem to have a significant contribution to the sediments of the lagoon, it can be a possible source for the sediments when considering storm drains (BP, B2, B3). Among the sampling sites, P24 (where rivers drains to the lagoon) seems to be the one with the most considerable influence of sewage (Fig. 6b). This observation is consistent with the fact that all rivers in the drainage basin flow to this point, including those that drain communities without sanitary infrastructure.

Therefore, the identification of potential sources becomes more difficult when there are complex sediment mixtures. In these cases, it is advisable to use a mix model. The relative contribution of the sources can be estimated by applying the following equations (Fry 2006):

$$\delta^{13}C_{orgSample} = f_a \times \delta^{13}C_{orga} + f_b \times \delta^{13}C_{orgb} + f_c \times \delta^{13}C_{orgc} \quad (1)$$

$$\delta^{15}N_{Sample} = f_a \times \delta^{15}N_a + f_b \times \delta^{15}N_b + f_c \times \delta^{15}N_c \quad (2)$$

$$1 = f_a + f_b + f_c \quad (3)$$

where f is the fractional contribution of each source a, b, and c.

If there are 3 sources and 3 equations, the solution is indicated reliably. However, mixing models can become indeterminate if there are more sources than biotracers. To assess which sources are relevant or representative to be used in the mixing models, the $\delta^{15}N \times \delta^{13}C_{org}$ plot should be evaluated (Fry 2013). Based on Fig. 6b, terrestrial, marine, and untreated sewage sources were considered relevant for the bottom sediment characterization in the RFL: terrestrial and untreated sewage in the drainage basin; Terrestrial, oil products, and atmospheric in the storm drains.

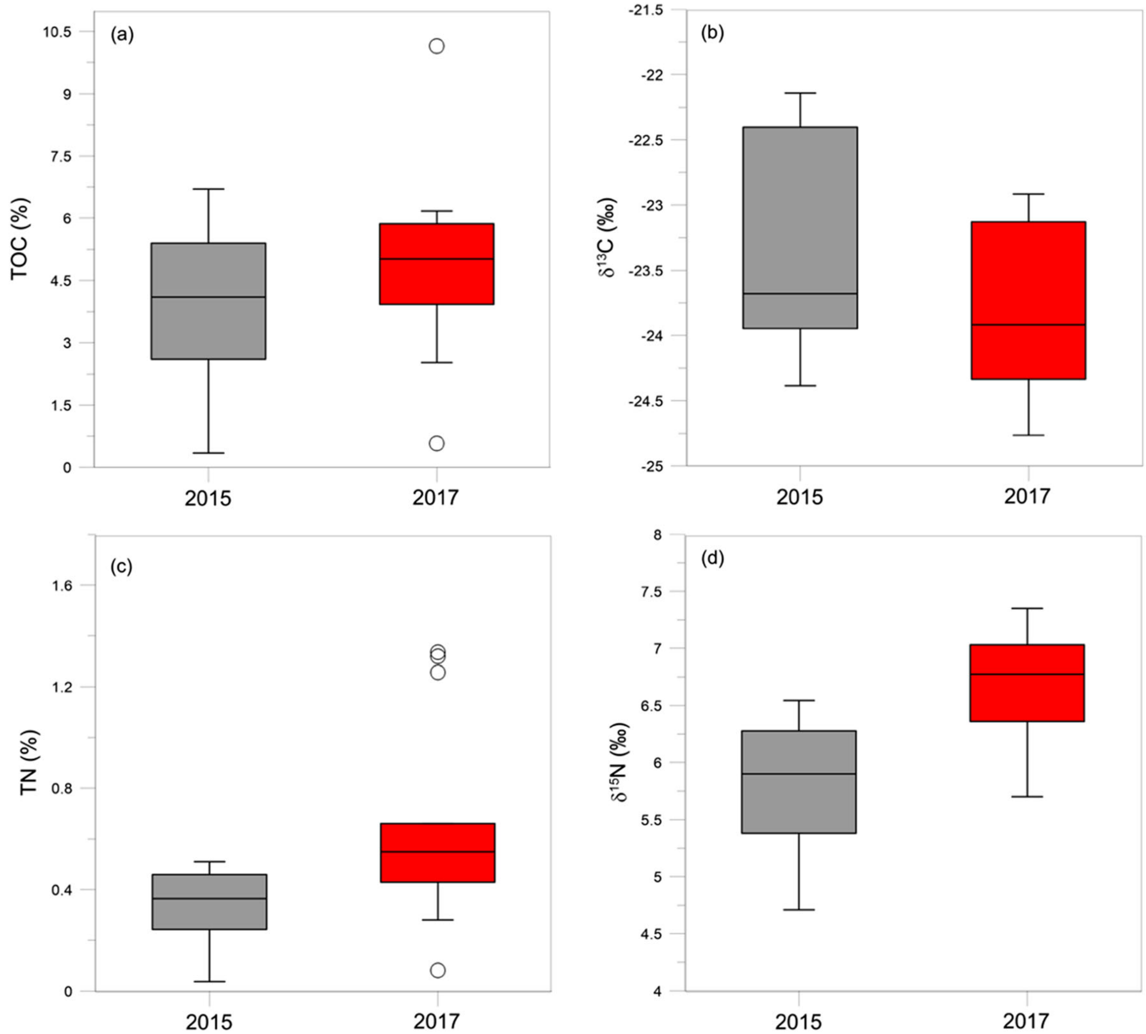


Fig. 4 Boxplot of (**a**) TOC (%), (**b**) $\delta^{13}C_{org}$ (‰), (**c**) TN (%), and (**d**) $\delta^{15}N$ (‰) in bulk bottom sediments from the Rodrigo de Freitas Lagoon in 2015 (gray) and 2017 (red). Symbol ° indicates outliers, i.e., values outside the limits

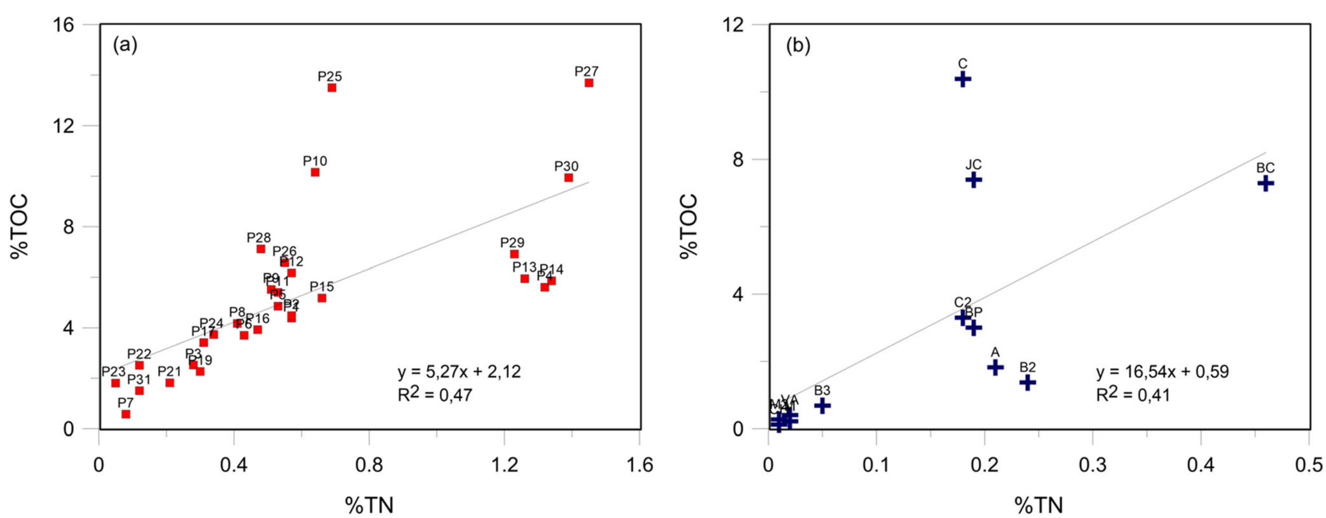


Fig. 5 Distributions of TOC (%) as function of TN (%). **a** Rodrigo de Freitas Lagoon and **b** drainage basin

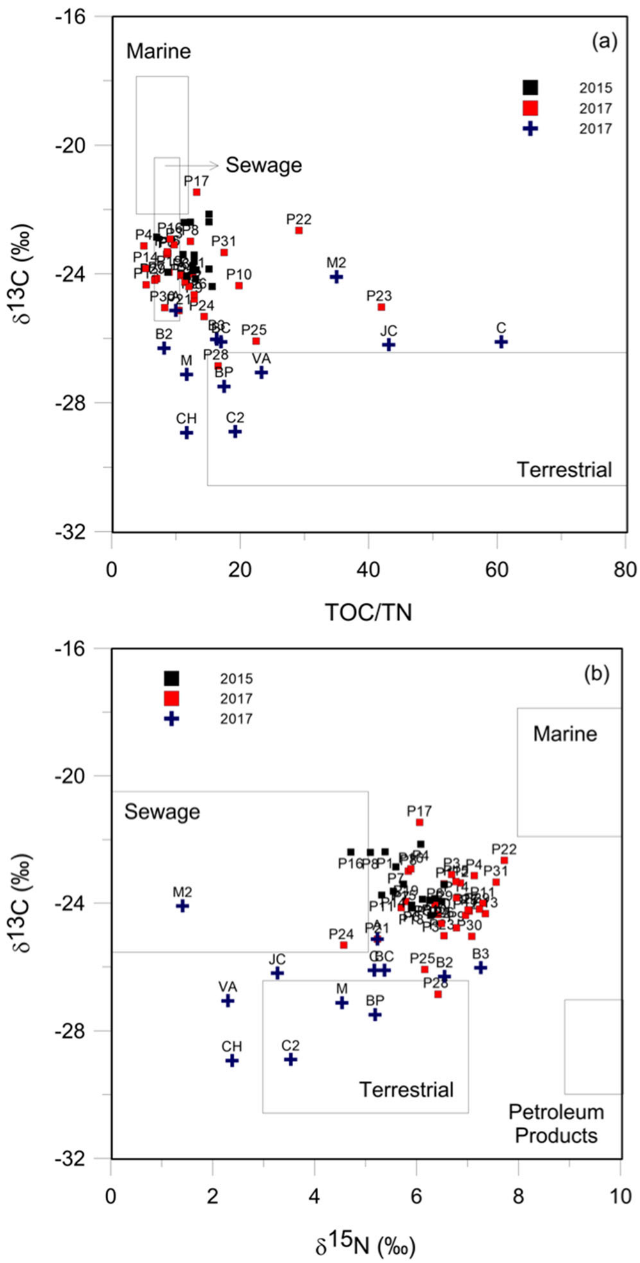


Fig. 6 Distributions of (**a**) TOC/TN × $\delta^{13}C_{org}$ and (**b**) $\delta^{15}N \times \delta^{13}C_{org}$. The symbol ■ represents the bottom sediments in the RFL (2015 in black and 2017 in red); + the sediments from the drainage basin (2017). Values used as a reference were taken from Table 2, Meyers (1994), Barros et al. (2010), and Rumolo et al. (2011)

The values of $\delta^{13}C_{org}$ and $\delta^{15}N$ for the potential organic matter sources adopted as reference in the mixing model are shown in Table 2. For the marine organic matter sources, $\delta^{13}C_{org} = -20‰$ (Carreira et al. 2002) and $\delta^{15}N = 9‰$ (Meyers 2003). For untreated sewage, $\delta^{13}C_{org} = -24.4‰$ and $\delta^{15}N = 2.5‰$. For terrestrial sources, $\delta^{13}C_{org} = -28‰$ and $\delta^{15}N = 5‰$. Once the petroleum product sources were apparently not significant in the lagoon and river samples (Fig. 6b), they are only considered as potential sources for the sewers ($\delta^{13}C_{org} = -8‰$ and $\delta^{15}N = 0‰$, Reiffarth et al. 2016), terrestrial, and petroleum products ($\delta^{13}C_{org} = -28.5‰$ and $\delta 15N = 9.5‰$).

For the channel and river samples, the marine contribution was considered negligible, and therefore, only terrestrial and sewage contributions were considered. When a negative value was obtained for a given source contribution, it was considered null, and the contributions from other potential sources were recalculated.

From the calculations of the average domestic sewage contribution from the mixing model predictions (Fig. 7) in 2015 ($n = 16$, mean = 32 ± 16%) and 2017 ($n = 29$, mean = 12 ± 13%), it is observed that there was a decrease in the untreated sewage releases after the LFR revitalization works.

It is noteworthy that the bottom layer sampled in 2015 was about 10 cm depth. Considering that RLF has a sedimentation rate of 0.75 cm/year (Loureiro et al. 2009) and that the dredging works in the lagoon were carried out between 2009 and 2015, it is possible to assume that the bottom sediment samples are older than 10 years. In turn, the bottom sediment samples collected in 2017 (up to 2 cm depth) have a maximum age of 2 years. Therefore, the decrease in the untreated sewage releases may be associated with both dredging works and implementation of a new underground drainage network. This intervention prevented rainwaters flow into the RL during the dry season. They started to be directed to the submarine outfall of Ipanema. Other interventions included actions to prevent clandestine sewage connections' underground drainage network, improving the water quality for the 2016 Olympic Games. Despite the decrease in the untreated sewage releases in the RFL, the decontamination actions were not enough to mitigate the organic matter pollution since the sewage is still an important pollution source.

The findings observed from Fig. 3d suggest that the higher sewage contributions are located in the western and southeastern sectors of the RFL. It is likely that most of the organic matter source is from the macroalga blooms due to eutrophication processes caused by sewage contaminations. Based on the results of the mixing model, it is possible to verify that the estimated source contributions to P17, for example, were 50% from sewage and 50% marine sources. This finding corroborates the observations referring to Figs. 3d and 6b.

The mixing model results for the sedimentary organic matter source contributions from water bodies in the RFL drainage basin (collected in 2017) showed a high contribution of untreated domestic sewage in rivers and channels (Fig. 8a), mainly M2 (Macacos River) and C (Cabeça River). CVA (Visconde de Albuquerque Street Channel) and CJ (Jockey Club Channel) show sewage contribution values of 25% and 47%, respectively. The Visconde de Albuquerque Street channel corresponds to the contribution of Rainha River (which drains the Rocinha Community, with little or no sanitary sewage infrastructure), and drains to the Jockey Club Channel (which drains to the RFL) and to the Leblon beach. These

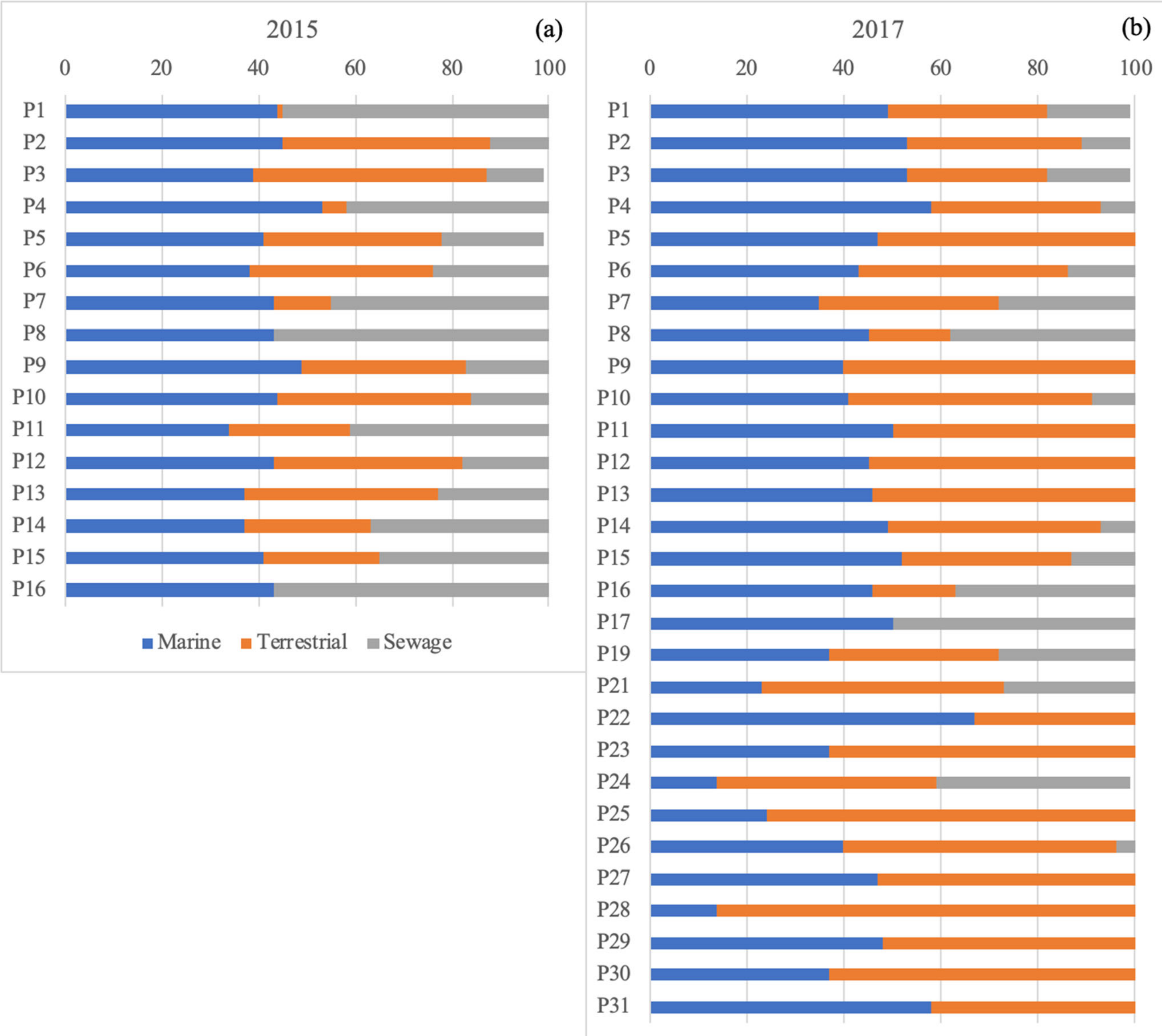


Fig. 7 Mixing model results for the sedimentary organic matter source contributions in the RLF in (**a**) 2015 and (**b**) 2017

results strongly indicate that these channels are important contamination sources in the coastal aquatic ecosystems from the southern part of Rio de Janeiro city. The sediment sampled in the Horto Waterfall (CH) did not show domestic sewage as a potential contribution source as expected, because it is in the environmental protected area of the Tijuca Rainforest. A similar result is observed for C2 (Cabeça River point 2).

For the sediments sampled in the storm drains around the lagoon, the mixing model results indicated that the B2 and B3 drains have an organic matter contribution from petroleum products (Fig. 8b). The BC (storm drain control) and the BP (fuel station storm drain) had a predominantly terrestrial contribution. The BC was the sampling point located far away from the fuel station influence. However, all the storm drains were located at an avenue with high traffic of motor vehicles.

Conclusions

The decontamination actions in the Rodrigo de Freitas Lagoon for the 2016 Olympic Games did not have significant effects to mitigate the organic matter pollution. Although a decrease in the untreated sewage releases into the lagoon between 2015 and 2017 was in fact verified, the domestic sewage still shows as a major organic pollution contributor in the RFL's bottom sediments. There are still points of illegal sewage releases. The rivers in the catchment remain highly polluted and are the main sewage sources in the lagoon. The surrounding storm drains have been contaminated by petroleum products, indicating that these contaminants are eventually drained into the lagoon. It is likely that most of the marine organic matter of marine is from the macroalga blooms due to eutrophication

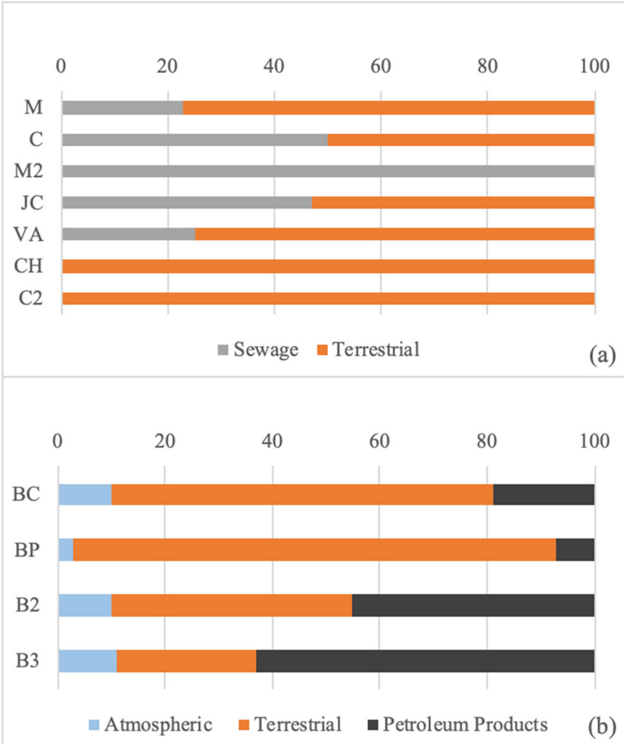


Fig. 8 Mixing model results for the organic matter source contributions in the (**a**) sediments from rivers and channels in the RFL's drainage basin and (**b**) storm drains in the RLF watershed

processes caused by sewage contaminations. However, this hypothesis requires further studies in future works.

These results are expected to provide important inputs to improve public health and basic sanitation services, avoiding improper wastewater management with the allocation of responsibilities according to the pollution sources.

Authors' contributions MV: conceptualization, methodology, validation, formal and statistical analysis, investigation, writing - original draft, writing - review and editing, visualization;

RMA: conceptualization, methodology, validation, writing - review and editing, visualization, resources; supervision, project administration, funding acquisition;

RGC: conceptualization, methodology, validation, writing - review and editing, visualization, supervision, project administration, funding acquisition;

MM: investigation, writing – review;

RC: formal analysis, investigation, writing – review;

JPF: investigation, writing – review;

DV: statistical analysis, investigation, writing – review;

HP: conceptualization, methodology, validation, writing - review and editing, visualization, supervision, project administration, funding acquisition.

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Compliance with ethical standards

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare that they have no competing interests.

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