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Formation of OSA and dispersion of polycyclic aromatic hydrocarbons in a tropical estuary as a tool in the prevention of environmental impacts: influence of the biogeochemical characteristics of the estuary

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Abstract The formation of an oil-suspended particulate material aggregate (OSA) is one of the weathering processes that occur after the spill of oil in marine environments, responsible for the dispersion of hydrocarbons. Oil and particle aggregates are formed from the interaction between small oil droplets and suspended particulate matter (SPM). In general, SPM are fine particles which may be inorganic minerals or organic particles in the water column. OSAs provide vertical dispersion of oil along the water column depending on the acquired density (buoyancy), and may remain near the surface, water column, or bottom of water bodies. The present study examines the formation of these aggregates through the laboratory simulation of an oil spill in the waters of the São Paulo river estuary. The main objective was to investigate the dispersion of polycyclic aromatic hydrocarbons (PAHs), verifying which estuary characteristics most influenced the formation of OSAs and in addition to determine the regions of probable ecotoxicological impact due to the negative buoyancy of the formed aggregate. The results show that there was greater dispersion to the water column, mainly of lighter PAHs, ranging from 85,804.05 ng g^{-1} (P11C) to 566,989.84 ng g^{-1} (P17C). The percentage of dispersed PAH concentration per experimental unit ranged from 9.90% in unit P2 to 75.27% in unit P18. The formation of OSAs was influenced mainly by salinity and chlorophyll *a*. As the most vulnerable regions, the impacts are one mouth (P2 and P4), one central region (P7, P8, and P10), and one source (P18).

Keywords Oil · Oil-suspended particulate material aggregates (OSAs) · Ecotoxicological impacts · Todos os Santos Bay

Introduction

Exploration, transportation, and refining of petroleum and its derivatives are the basis of the global energy sector, but it is tied to environmental risks and accidents, bringing damages to the ecosystems and populations that live there (Siqueira et al. 2004; Moraes 2007; ITOPF 2019). Oil can be released into the marine environment through routine or accidental activities, including drilling, refining, storage, transportation, and waste

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management. It is important to note that the impact of this type of oil can be extended to depend on some factors such as the volume and type of oil spilled and the characteristics of the environment (Wang et al. 2008; Gong et al. 2014; Moreira et al. 2015).

After an oil spill in a marine environment, some chemical, physical, and biological intemperate processes occur. The intensity of these processes varies according to the characteristics of the environment and the oil spilled and will influence the rate of degradation and persistence of these compounds in the environment (Khelifa et al. 2002; Agarwal and Liu 2015; NOAA 2017).

Among these processes is the formation of oil-suspended particulate material aggregates (OSAs), microscopic in size and stable for weeks, months, or years, which act to reduce damage through natural dispersion processes and determine the fate of oil in the water column (Bragg and Owens 1995; Bragg and Yang 1993; Lee et al. 2003; Owens and Lee 2003; Sun and Zheng 2009; Reyes et al. 2014; Moreira et al. 2015; Loh and Yim 2016; Zhao et al. 2016; Miranda et al. 2016; Cai et al. 2017; Gustitus et al. 2017, Rios et al. 2017; Gustitus and Clement 2017; Martins et al. 2019). Its occurrence has been studied since 1941 by Poirier and Thiel (1941), who called this aggregate a mixture of oil, sediment, and sea water. The first findings of the formation of OSA in the field and greater repercussion of the thematic came from the accident of the Exxon Valdez, in which the cleaning of coastal regions until then contaminated by oil stains was noticed. After the mass balance, part of the oil had been dispersed by an unidentified process, and further analysis confirmed the formation of OSA, observed and later verified also in the Sea Empires spill (Bragg and Yang 1993; Lee et al. 1997).

In summary, oil and particulate aggregates are formed from the interaction between small oil droplets and suspended particulate matter (SPM). In general, SPM are fine particles, $< 10\ \mu m$ (Sun and Zheng 2009), and may be inorganic or organic particulates in the water column (Gustitus and Clement 2017).

Once formed, OSAs not only disperse the oil but also help in the decision-making and management of areas impacted or that may be impacted by activities linked to the oil industry, indicating which regions have the greatest ecotoxicological impacts in case of oil spill (Moreira et al. 2015; Miranda et al. 2016; Rios et al. 2017; Martins et al. 2019), and intensify the biodegradation of the compounds by hydrocarbonoclastic organisms (Lee et al. 2003; Sergy et al. 2003). The vertical fate of these aggregates will depend on their buoyancy, which, depending on the density obtained, can be positive (surface), neutral (water column), or negative (water bottom) (Loh et al. 2014).

The amount of oil dispersed and the size and type of OSA are controlled by environmental variables such as water salinity (Lee et al. 2002; Sun and Zheng 2009; Danchuk and Willson 2011; Gong et al. 2014; Miranda et al. 2016); the type, size, and concentration of suspended particulate material (Guyomarch et al. 2002; Khelifa et al. 2002; Ajijolaiya et al. 2006; Gong et al. 2014; Miranda et al. 2016); turbulence (Delvigne and Sweeney 1998; Payne et al. 2002; Stoffyn-Egli and Lee 2002; Sun et al. 2010; Sun et al. 2014); oil characteristics (Bragg and Owens 1995; Khelifa et al. 2002; Bandara et al. 2011; Gong et al. 2014); and the concentration of organic matter (Moreira et al. 2015).

Polycyclic aromatic hydrocarbons (PAHs) are a constituent of petroleum and can be dispersed by OSA. They are formed by two or more aromatic rings, single or fused with a pair of carbon atoms shared between the rings in their molecules. Due to the lipophilic character and high coefficient of water-octanol partition, added to the concentration of organic matter present in the suspended particulate material, the PAHs tend to aggregate to the SPM forming the OSA, dispersing along the water column and to the bottom (Li et al. 1995; Moreira et al. 2015; Abdel-shafy and Mansour 2016; Zheng et al. 2016).

In this context, the present research proposes to study the dispersion of the polycyclic aromatic hydrocarbons (PAHs), priority in environmental studies, from the formation of OSAs in the São Paulo river estuary, Todos os Santos Bay, Bahia. Thus, this is to understand how the characteristics of the estuary contribute to this, indicating the possible ecotoxicological impacts. In this way, this presents itself as a guiding tool that assists decision-making in case of oil spill in the studied region, contributing to the management of the impacted area. To this end, the following specific objectives were established: analyze the dispersion of the contaminant in the bottom and in the water column of the studied estuary; to determine the degree of influence of the studied estuary geochemical characteristics on the formation of OSAs; indicate the regions of possible biological impairment in an adverse oil spill scenario across ecotoxicological limits for PAHs; and generate continuous surface maps with the results of the dispersion of PAHs along the column and bottom of the studied estuary to apply them as a guiding tool in decision-making.

Materials and methods

Study area and sampling sites

The estuary of the São Paulo river is in the Todos os Santos Bay, Bahia, Brazil (12° 50″ S–38° 38″ W). This bay has semi-diurnal tidal variations (Lessa et al. 2001) and it is the second largest bay in Brazil. It is surrounded by port terminals, industrial activities (Hatje and de Andrade 2009), and 14 districts that account for an average of 3.6 million people (IBGE 2010).

The studied estuary is in the São Paulo river basin and has a drainage area of 37 km^2, an average flow of 0.3 m^3 s^{-1}, a total length of 17 km, and some of its mangrove banks (Bahia 2000). In the geological context, it is contained in the Recôncavo Basin, and there is predominance of sedimentary and clayey lithotypes. In the coastal region, there is accumulation of clay-silt sediments (Bahia 1994). The climate of the region is humid and has an average annual rainfall of 1800 mm, in which the months of highest rainfall are from April to June (Bahia 1994; Carvalho 2007; INMET 2019).

The map of the study region contains the sampling stations as well as illustrates important characteristics in the region (Fig. 1). The region near the upper estuary is The Landulpho Alves de Mataripe Refinery and the region in the lower estuary is the district of Passé. Such characteristics make this estuary vulnerable to environmental impacts due to the activities in its surroundings (PETROBRAS/FUNDESPA 2003; Moreira et al. 2013).

Sampling and processing of samples

The previous sampling planning was carried out to determine the collection stations with the aid of satellite images, the software Arcgis10.4.1, and bibliographic review of the studied area. In addition to this, pre-field for area recognition and sample collection for laboratory tests was performed. According to the results found in the OSA training tests, 18 sampling stations were defined along the São Paulo river estuary with 10% field triplicate.

Sampling was carried out on May 15, 2018, in the lower tide of syzygy in the São Paulo river estuary, Todos os Santos Bay, Bahia, alternating between the right and left margins and the center of each sector of the estuary (Fig. 1). The material was collected in two boats, the first from the mouth to the center of the estuary and the second from the source to the center of the estuary, in order to ensure that the samples were collected under the same conditions.

At the sampling stations, surface water samples were collected for the analysis of particulate organic carbon (POC), chlorophyll *a*, polycyclic aromatic hydrocarbon (PAH) concentration and for the OSA formation and hydrocarbon dispersion experiment. Samples were stored in containers previously decontaminated with Extran® 10%. The containers intended for the analysis of PAHs and experiment OSA formation simulation were also decontaminated with dichloromethane (Merck, Darmstadt, Germany). In each season, 4 bottles (1 L) were collected, except for P2, P8, P10, and P15 stations which were sampled in triplicate.

All material collected was kept under refrigeration in the field until the arrival at the Laboratory of Excellence in Geochemistry (LEPETRO), at the Federal University of Bahia, where they were refrigerated. In the following days, the OSA training experiments were carried out. In addition, the physicochemical parameters, temperature (°C), potential hydrogen (pH), salinity (PSU), dissolved oxygen (mg L^{-1}), and turbidity (NTU), were measured in the field at each sampling station using the multiparameter probe of the brand Horiba, model U50.

Analytical methods

To compose the results and to reach the objective of correlating the RSP estuary characteristics (salinity, POC, chlorophyll *a*, and SPM) with the formation of OSA and dispersion of PAHs along the RSP estuary (São Paulo river), the characterization geochemistry is the same, using the methodology described in Table 1.

Salinity was measured in situ and the concentration of the particulate material in suspension was obtained by vacuum filtration of the water collected using GF 2 (0.45 μm) glass fiber membrane previously calcined.

To assure the analytical quality of the generated data, all chemical analyses were performed containing 10% of the following: bench blank, bench triplicate, and field triplicate. The glassware used was previously decontaminated in a 10% Extran® bath and calcined in the SP-1200 muffler (Splabor) for 4 h at 400 °C to remove possible interferences.

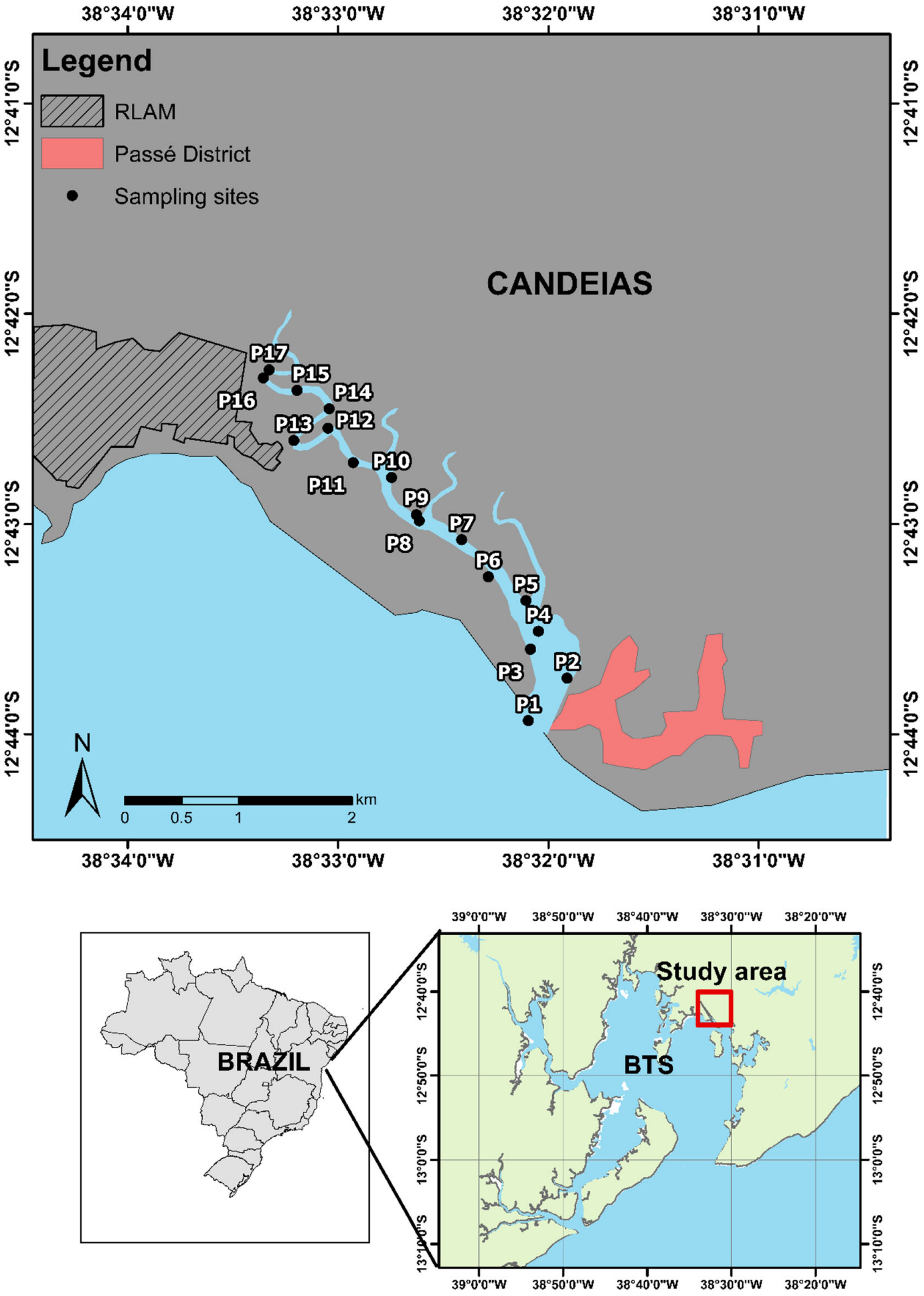

Fig. 1 Study area and sampling stations, with location of the São Paulo river estuary, Todos os Santos Bay, Bahia, Brazil, with vicinity of the district of Passé and Ladulpho Alves de Mataripe Refinery. Source: modified by the author of CPRM 2018.

To evaluate the quality of extraction and recovery of the aromatic compounds studied, a surrogate standard, *P*-terphenyl D14, was used in all samples, with an accepted recovery of 70–120%. The same was added at the beginning of the extraction process in the area characterization samples and in the samples resulting from the OSA formation simulation experiment. The recovery rate of the surrogate in the samples ranged from 60 and 134%, except for the P6F simulation unit that obtained recovery of 46%. The blanks were submitted to the same analytical processes of the other samples and presented results below the DL, being considered contamination free.

To calculate the detection limit (DL), seven replicates were fortified with a mixture of the 16 priority PAHs. The DL was calculated by multiplying the Student's *t* test value (nc = 99%; $n-1 = 3.1417$) by the standard deviation (SD) of the concentration reported for each analyzed compound ($\mathrm{DL} = t_{n-1} \times \mathrm{SD}$) (Wade and Cantillo 1994). DL values ranged from 1.13 to 0.83 μg L^{-1}.

Experiment of forming oil-suspended particulate matter aggregate

Simulation experiments were carried out in LEPETRO at the Federal University of Bahia. The experiment was carried out five times and each of them had 8 Erlenmeyers on a reciprocating shaker table, model MARCONI MA 570, subjected to agitation at 126 cycles per minute. The simulations contained a blank made with ultrapure water extracted with dichloromethane (Merck, Darmstadt, Germany), 10% field triplicate, and 10% triplicate bench. The simulation units were coated with a dark material to prevent the loss of compounds by photooxidation during the experiment and sealed at the exit to avoid losses.

Table 1 Analytical methods used to determine the geochemical characteristics of the São Paulo river estuary

Parameters	Methods used
Chlorophyll *a*	Adapted from APHA 1998;
PAHs	Adapted from Cavalcante et al. 2008; Cotta et al. 2009 and Sousa 2016
Organic carbon in particulate matter	Strickland and Parsons (1972)

Source: the author, 2019

Each simulation unit represented a sampling station and contained 250 mL of water from the São Paulo river estuary, with the main characteristics maintained. These were added with 50 mg of oil from the Campos basin, Macabu and Coquinos formation, well 6- CHT-04- ESS, simulating a spill. The oil profile and distribution of PAHs, as well as petroleum characterization information, used in this experiment are shown in Fig. 2 and Table 2.

After each experiment, 50 mL of the column and 50 mL of the Erlenmeyer bottom were removed and then reserved and frozen in 100-mL amber bottles for extraction. After removing the aliquots, knowing that when adding the oil from the Campos basin in the simulation units and connecting the reciprocating agitator table, a certain amount of the oil agglutinated the walls in some Erlenmeyer, and the unreacted oil was counted systematically and abated the initial value added, obtaining a real dispersion response for each simulation unit.

The methodology used to carry out this work was proposed by Khelifa et al. (2002) adapted from Moreira collaborators (Moreira et al. 2015), and since then it has been adapted for different applications of the OSA studies in Brazil (Silva et al. 2015; Miranda et al. 2016; Rios et al. 2017) and more recently adapted by Martins et al. (2019), in which more field-oriented responses are sought, without the addition of SPM and use of artificial saline water, maintaining as much as possible the characteristics of the environment collected closer to the reality of the studied environment.

Extraction and determination of polycyclic aromatic hydrocarbons

The samples obtained after the experiment were extracted using the methodology adapted from Khelifa et al. (2002), which has been successively used in studies within this area (Silva et al. 2015; Silva et al. 2015; Miranda et al. 2016; Rios et al. 2017). Briefly, the sample is placed in an extraction funnel (250 mL) along with 50 μL of the surrogate standard (*P*-terphenyl D14, 2000 and 500 μg L^{-1}) and 50 mL dichloromethane solvent (Merck, Darmstadt, Germany). After stirring for 30 s, it is then sent to the vacuum filtration process. The above two steps are repeated twice, totaling three shakes and filtrations. At each filtration where the filtrate accumulates in the kitassate and at the end is transferred to a round bottom flask, the extract is next

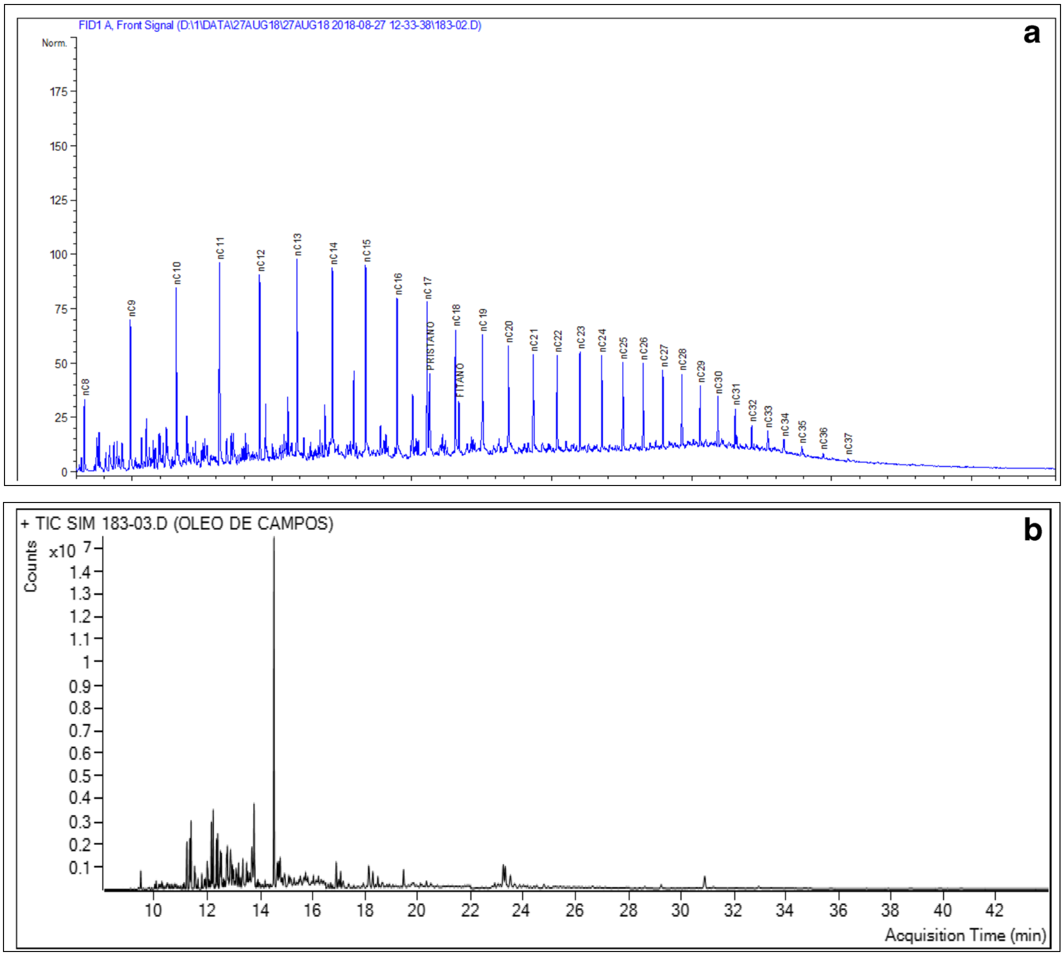

Fig. 2 Chromatographic profiles of the Campos basin oil. **a** Total hydrocarbon distribution profile. **b** Distribution profile of polycyclic aromatic hydrocarbons. Source: the author, 2019

Table 2 Properties of oil from the Campos basin

Property	Results
Density (g mL^{-1})	0.88^{a}
Viscosity (m Pa s)	36.44^{a}
Pristane (kg mg^{-1})	3249.84^{b}
Phytane (kg mg^{-1})	2271.42^{b}
UCM (kg mg^{-1})	116,014.80^{b}
TPH (kg mg^{-1})	351,826.50^{b}
Pristane/phytane	1.43^{b}
Pristane/n-C$_{17}$	0.47^{b}
Phytane/n-C$_{18}$	0.35^{b}
∑PAHs (ng g^{-1})	603,895.82^{b}
∑PAHs lights (ng g^{-1})	500,357.70^{b}
∑PAHs high (ng g^{-1})	103,538.10^{b}

Source: ^{a} Assunção, 2014; ^{b} the author, 2019

subjected to a rotary evaporator model R210 (Butch, Switzerland). The concentrated extracts are passed through a silica chromatographic column using 40 mL of the dichloromethane/hexane mixture (2:1) (Merck, Darmstadt, Germany), added to separate the aromatic fraction, further concentrated, transferred to microvials, and added to 200 μL.

Determination of the 16 priority PAHs was performed on an Agilent 7890B GC system gas chromatograph coupled to an Agilent 5977A mass spectrometer (GC/MS) under the singular ion monitoring (SIM) mode. The characteristics of the silica capillary column used were HP-5MS and 60 m × 250 μm × 0.25 μm film thickness. The initial oven temperature was 100 °C that varied at intervals of up to 300 °C. The temperature of the ion source was 230 °C and the quadrupole 150 °C. The entrainment gas used during the analyses was highpurity helium with a flow rate of 1 mL min^{-1}. The internal calibration of the equipment was obtained through five points with a mixture of the 16 priority PAHs with concentrations ranging between 10 and 200 μg L^{-1}. The accepted correlation coefficient for these curves was 0.99. The surrogate recovery rate in the samples varied between 60 and 134%, except for the P6F simulation unit that obtained recovery of 46%.

Treatment of data

The Pearson correlation was performed using Statistic software for Windows, version 7.0 of Statsoft Inc., and dispersion analyses were performed using the free software version R, version 3.5.1, with the aid of the Coorplot and Graphics packages. The maps were plotted using ARCGIS, version 10.3.1, applying the inverse distance weighting (IDW) interpolation technique.

Results and discussion

Dispersion of PAHs as a function of the formation of OSA along the water column and bottom of the simulation units

The dispersion of the ΣPAHs along the simulation units can be observed in Fig. 3; each simulation unit was plotted on a graph where the code P1C stands for station simulation station P1 column, P1F stands for station simulation unit sampling P1 background, and so on.

Observing Fig. 3, it can be seen that P17 was the one that most formed OSA with neutral buoyancy, dispersing 566,989.84 ng g^{-1} of PAHs to the water column. In general terms, there were larger dispersions for the water column except for the simulation units P2, P4, P7, P8, P14, and P18, which formed OSA with negative buoyancy.

The percentage of the concentration of ΣPAHs dispersed per unit of experiment ranged from 9.90% in unit P2 to 75.27% in unit P18, and the mean value of ΣPAHs dispersed in the 18 experimental units was 36.49%. The dispersion of PAHs as a function of the formation of OSA in this work was satisfactory and can be seen in Table 3, which contains the percentage of PAH dispersion as a function of the concentrations obtained in GC-MS. These results are notorious and relevant, evidencing that the aggregates of suspended particulate oil play an important role in the dispersion of total hydrocarbons (Khelifa et al. 2002; Lee et al. 2003; Owens and Lee 2003; Sun and Zheng 2009; Loh and Yim 2016; Moreira et al. 2015; Zhao et al. 2016; Miranda et al. 2016; Cai et al. 2017; Gustitus et al. 2017; Rios et al. 2017; Gustitus and Clement 2017; Martins et al. 2019) and also specifically polycyclic aromatic hydrocarbons.

Analysis of PAH dispersion as a function of molecular weight

To understand the PAH dispersion as a function of the number of rings they have, the dispersion was separated between the polycyclic aromatic hydrocarbons having low molecular weight and high molecular weight. Analyzing Fig. 4a, low molecular weight PAHs were found to have higher concentrations in the water column than at the bottom; column variation was quantified between 48,868.13 ng g^{-1} (P2) and 467,271.50 ng g^{-1} (P17) while background was 36,703.76 ng g^{-1} (P6) and 395,060.80 ng g^{-1} (P18). With respect to Fig. 4b, it is noted that the variations found in the dispersion of the high molecular weight PAHs in the column were 9535.04 ng g^{-1} (P2) and 99,718.35 ng g^{-1} (P17) and background 7321.78 ng g^{-1} (P6) and 124,137.80 ng g^{-1} (P 18). In both situations (Fig. 4a and b), there is a tendency of increasing the dispersion of the lower estuary to the middle estuary, followed by a decrease and increase in the regions closer to the upper estuary.

It was expected that there would be a greater dispersion of the heavy polycyclic aromatic hydrocarbons rather than the light ones in both situations (column

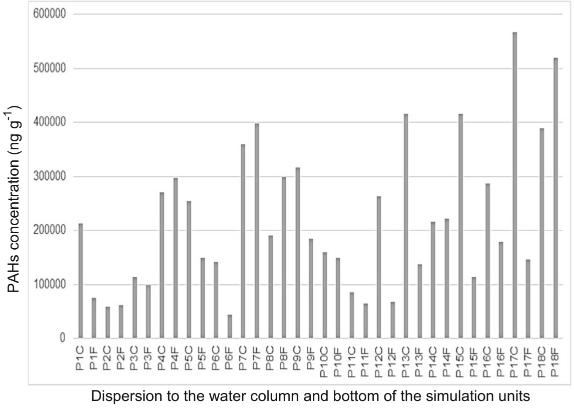

Fig. 3 The sum of the total PAHs distributed between the column and the bottom of the simulation units as a function of the OSA formation; the abscissa axis represents the simulation units and the ordinate axis represents the concentration of dispersed PAHs (ng g^{-1}). Source: the author, 2019

Table 3 Percentage of dispersion of ΣPAHs from the formation of OSA in the São Paulo river estuary in the 18 experimental simulation units

UE	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**
% PD	23.88	9.90	17.67	47.06	33.38	15.46	62.89	40.61	41.52
UE	**P10**	**P11**	**P12**	**P13**	**P14**	**P15**	**P16**	**P17**	**P18**
% PD	25.51	12.53	27.37	45.83	36.32	43.86	38.66	59.06	75.27

UE experimental unit, *%PD* percentage of dispersed ΣPAHs. Source: the author, 2019

and bottom), due to the high partition coefficient of octanol-water, so that each added aromatic ring decreases to the solubilities of the same ones in water, and thus the lighter ones are more soluble in water and the heavier ones would tend to aggregate with SPM (Sims and Overcash 1983; Yalkowsky et al. 1994; ATSDR 1995); however, it was quantified that higher values of light scattered PAHs as a function of the formation of the OSA, suggesting that by removing the aliquots the higher molecular weight PAHs were addition to the SPM that soon saturated, while those with lower molecular weight were diluted in water and also added to the SPM (Gearing, Gearing, Pruell, Wade and Quinn 1980), resulting in a greater dispersed volume. In the Campos basin oil used in the experiment, it contained high amounts of light hydrocarbons (500,357.70 ng g^{-1}) when compared with heavy ones (103,538 ng g^{-1}), approximately 5 times more in 25 mg, whereas in the experiments, 50 mg of oil was used, which may have corroborated the results.

Correlation between the characteristics of the São Paulo river estuary and the formation of oil-suspended particulate material aggregates

The Pearson correlation (Table 4) shows which characteristics of the São Paulo river estuary analyzed had a greater positive and negative influence on the formation of OSA and dispersion of PAHs.

In this study, neutral buoyancy was more strongly influenced by salinity and chlorophyll *a*, the first negatively and the second positively, the higher the average salinity, the smaller the dispersion and the stations with the highest chlorophyll concentrations obtained the higher the OSA formation in the water column. There was a weak negative correlation with the POC, differing from the results found by Moreira and collaborators (Moreira et al. 2015) in the same estuary; this difference possibly is because in their experiments, sediments and not the SPM of the river were used, and in addition, the concentrations of the sediment used by them were significantly higher than those found in the present study.

In relation to OSAs with negative buoyancy, the most significant correlations were also with chlorophyll *a* and salinity, respectively, influencing positively and negatively.

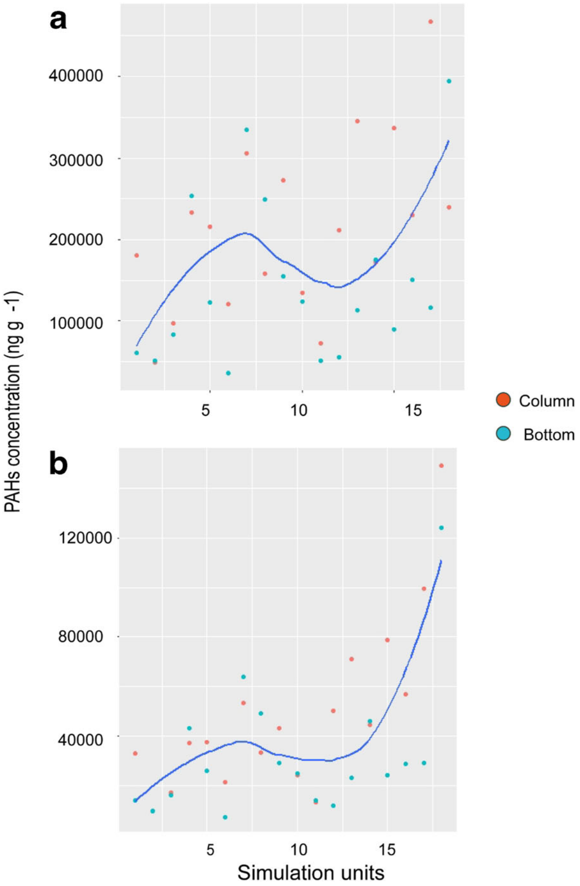

Fig. 4 Scatter plot of PAHs by OSA formation, where the abscissa axis represents the sampling stations and the ordinate axis represents the concentrations of PAHs (ng g^{-1}). **a** PAHs with low molecular weight along the column and bottom. **b** PAHs with high molecular weight along the column and bottom. Source: the author, 2019

Suspended particulate matter showed weak negative correlation with the dispersion of PAHs for both the column and the bottom of the simulation units, but in the column, this correlation was stronger than in the background. Previous works state that the increase in suspended particle concentration increases the dispersion of PAHs (Ajijolaiya et al. 2006; Sun and Zheng 2009; Moreira et al. 2015; Miranda et al. 2016); however, this has not been elucidated in this. By analyzing the correlations, this fact can be explained because in the other studies, the influence of other environmental factors that may influence the formation of OSA was not studied, or because of the higher concentrations of SPM used in these artificially increased studies (Ajijolaiya et al. 2006; Sun and Zheng 2009; Moreira 2014; Miranda et al. 2016).

Chlorophyll *a* positively influenced the formation of OSA with both neutral buoyancy (0.65) and negative buoyancy (0.53), being the highest positive correlation found in this study, being the main contributing factor for the formation of OSAs and dispersion of PAHs. These particles interacted with the oil to form OSAs. These interactions have been described in other studies (Boehm and Quinn 1974; Gearing et al. 1980; Wade and Quinn 1980; Passow et al. 2012), and they occur because phytoplankton produce extracellular polysaccharides (EPS) that help in the union of the surfaces as a function of their capacity to form nanogels of colloidal size with properties of nanofibers, with adsorptive capacity for hydrocarbons (Passow et al. 1994; Loh and Yim 2016).

Previous works claim that salinity contributes to the formation of aggregates through electrostatic actions. However, until a critical salinity in which the formation of OSA will stabilize, this value depends on the type of oil and characteristics of the SPM (Le Floch et al. 2002; Khelifa et al. 2003; Khelifa et al. 2005).

The salinity measured in the present study varied between 22.00 and 39.4 PSU, the regions where the lowest values of salinity were measured and where the highest concentrations of OSAs occurred. It is suggested that the higher salinities associated with the other characteristics of the estuary influenced negatively the formation of OSA and dispersion of PAHs, mainly because the biogeochemical parameter chlorophyll *a* was determinant in the formation of OSAs in the present study and in this context to densities, and communities diversity phytoplankton species decrease as salinity increases due to the stresses caused by them.

Even when simulated at low tide, lower ocean water influences the measured values of salinity that were high until the sampling station P14, reaching approximately 40 PSU; however, the salinities measured from stations P15 to P18 ranged from 20 to 30 PSU, and these stations were also where there were larger OSA formations. In summary, salinity values above 30 PSU, under the conditions of this experiment, decreased the formation of the aggregates and the salinity values found in the regions with the highest dispersion of PAHs are within the range of optimum salinity that contribute to the formation of OSA (Lee et al. 2002; Sun and Zheng 2009; Danchuk and Willson 2011; Gong et al. 2014; Miranda et al. 2016).

Le Floch et al. (2002) tested the dispersion of oil from the OSA with salinity of 0–35 PSU and its results showed that salinity positively influences the OSA; however, it did not establish an ideal salinity threshold since it can vary according to the characteristics of oil and SPM, and in the present study, salinities close to 24.75 PSU are more efficient for OSA formation, and higher values associated with the characteristics of the studied region and oil used in the experiment may decrease oil-SPM aggregation; however, it does not make it null.

The energy of mixing, or turbulence, breaks the oil spot into smaller droplets and keeps the particles suspended; it is a key factor in the formation of OSA (Sun et al. 2014) along with other environmental characteristics mentioned above. In the present study, the mixing energy remained constant at the ideal frequency and simulates the frequency of the region studied, which is equivalent to 126 cycles per minute at the reciprocating table. The temperature is also a key factor in the formation of aggregate microscopes (Delvigne 1887; Khelifa et al. 2002; Danchuk and Willson 2011) and remained constant throughout the experiment, 25 °C a common temperature in tropical environment. Due to constancy, these two variables did not enter correlation analysis.

Finally, the environmental parameters that regulate the formation of OSA established in later works were influencing the dispersion in the São Paulo river estuary. However, the strongest influences were salinity (negative) and chlorophyll *a* (positive).

Table 4 Pearson's correlation between the estuarine variables and the formation of OSA with dispersion of PAHs for column and bottom

	POC	Chlorophyll *a*	Salinity	SPM	PAHs C	PAHs B
POC	1					
Chlorophyll *a*	0.16	1				
Salinity	−0.13	*−0.61*	1			
SPM	−0.14	−0.25	0.40	1		
PAHs C	−0.15	*0.65*	*−0.63*	−0.47	1	
PAHs B	−0.01	*0.53*	−0.46	−0.38	0.38	1

Numbers in italics indicate a significant correlation with $p < 0.05$; the others indicate non-significant correlations with $p > 0.05$; *PAHs C* polycyclic aromatic hydrocarbons dispersed into the water column, *PAHs B* polycyclic aromatic hydrocarbons dispersed to the bottom. Source: the author, 2019

OSA as an ecotoxicological tool in predicting and preventing environmental impacts

Some authors state that OSA is an advanced cleaning method that can be aided by other techniques such as the relocation of oiled sediments to areas of greater turbulence (Surf Washing) and thereby accelerating the interactions between oil and suspended fine particles or by applying a sediment sludge directly to the oil slick (Owens 1998; Sergy et al. 1999; Lee et al. 2003; Gustitus and Clement 2017). Results of an experimental spill performed by Sergy et al. (1991) demonstrate and quantify that the mechanical relocation of sediments significantly accelerated the rate of oil removal through the formation of OSA. However, in situ, if sediments are added, it is advisable to do so after the time required to volatilize the lighter compounds, approximately 5 h; otherwise, they can be transferred to the water column without volatilizing naturally (Yin et al. 2015).

In Brazil, however, the main research carried out seeks to use the knowledge of the dispersion of the OSA to guide and prevent environmental impacts mainly from laboratory experiments that simulate the environments that are in a situation of vulnerability to oil industry accidents. The results found may be applied to management of these areas. This knowledge can help you make decisions in a possible oil spill scenario (Moreira et al. 2015; Miranda et al. 2016; Martins et al. 2019).

It is known that the dispersion of OSAs in the water column increases the biodegradation (Bragg and Owens 1995; Guyomarch et al. 1999; Omotoso et al. 2002; Owens and Lee 2003; Sun and Zheng 2009) and, however, increases ecotoxicity in the aquatic ecosystem (Muschenheim and Lee 2002).

Studies show that in the simulation units where the formation of the OSA was formed, there was also an increase in the number of bacteria in the water column over time as a function of the formation of the aggregates. This fact was corroborated by the depletion of oxygen, indicating that the bacteria were accumulating in the region where it had the highest concentration of the contaminant that served as food source for these microorganisms (Jezequel et al. 1999). In addition, the formation of aggregates from suspended particulate material and a crude oil stimulated bacterial growth, rate, and extent of hydrocarbon degradation. It was found that only 25% of the total concentration of the fraction of *n*-alkanes (*n*-C15 to *n*-C35) remained in the experiments where the formation of the aggregate occurred, whereas in the control experiment, there was a concentration of 48% with respect to the final concentration that was 8% while in the control experiment, it was 25% (Weise et al. 2010).

In an experiment carried out in 1996 in the laboratory, it was confirmed that the oil and SPM interactions stimulate the microbial activity in the water column increasing both the rate and extent of the oil degradation (Lee et al. 1996).

In this context, the São Paulo river estuary regions, in a scenario of spills under the simulation conditions of the present study, would present higher concentrations of PAHs dispersed along the column mainly in the source region (Fig. 5a), and these compounds can be biodegraded by microorganisms (Fitzpatrick et al. 2015).

Hydrocarbons dispersed to the bottom by OSA are hardly biodegraded (LOH et al. 2014). Although there is a higher density of microorganisms in the suspended particles than in the water and even if they are more

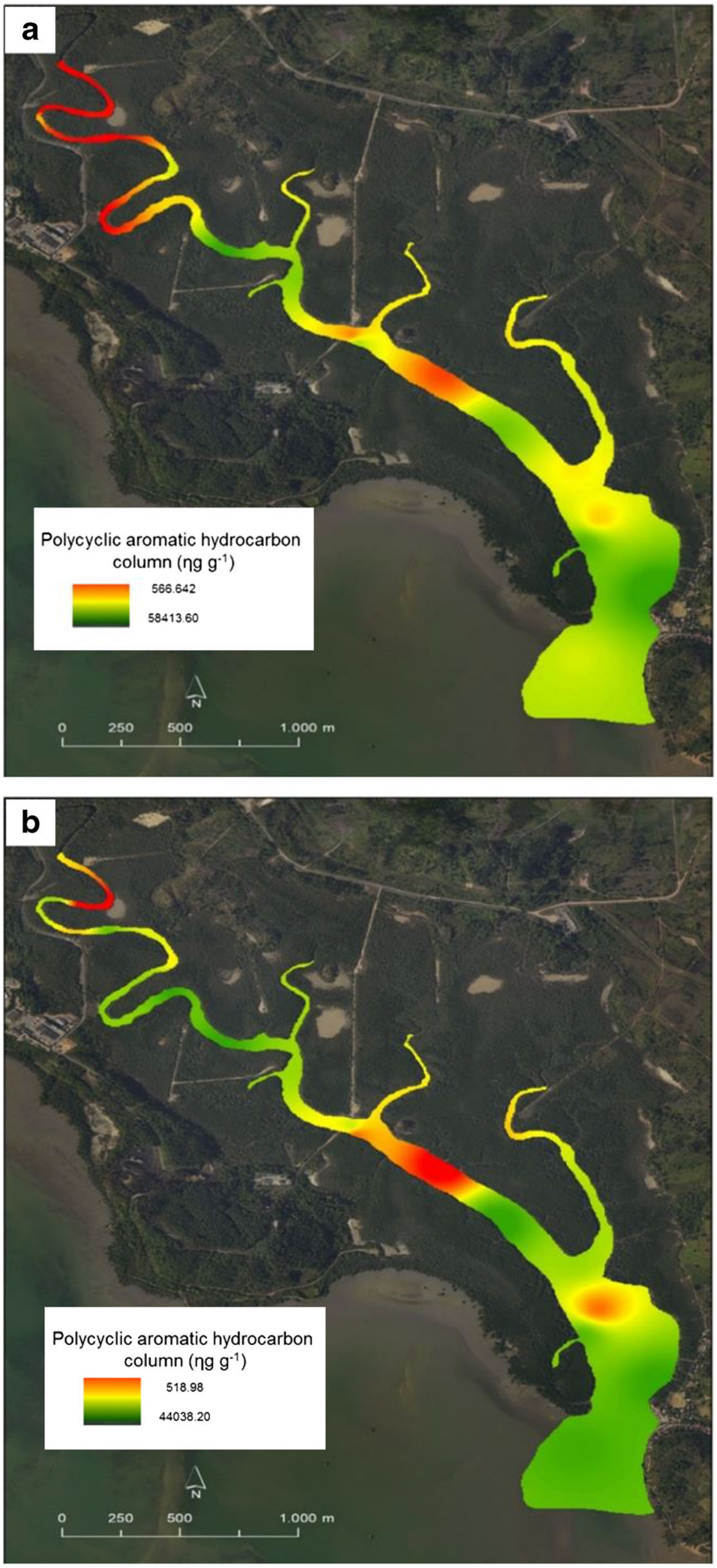

Fig. 5 Maps developed from the formation of OSA and dispersion of PAHs. **a** Dispersion along the column. **b** Scattering along the bottom. Source: the author, 2019

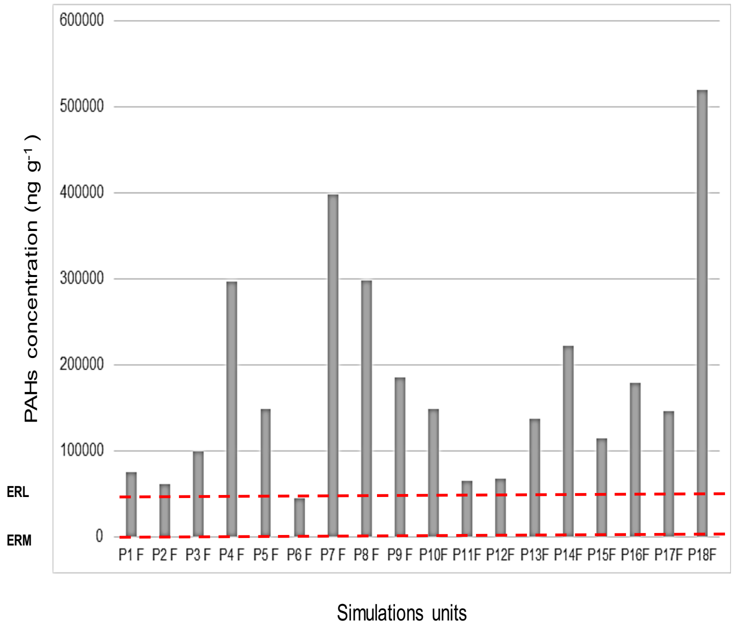

Fig. 6 Polycyclic aromatic hydrocarbons dispersed to the bottom of the simulation units and their limits of ecotoxicological effects, the abscissa axis represents the simulation experimental units and the ordinate axis represents the dispersed mass (ng g^{-1}). Source**:** the author, 2019.

metabolically active than the suspended ones, in the bottom region, this density decreases significantly (Harvey and Young 1980; Van Loosdrecht et al. 1990); in this way, the OSAs with negative buoyancy cause immediate impacts to the benthic organisms and over time can cause more aggravating impacts due to the change of the environmental conditions that consequently alter the bioavailability of the contaminant. Therefore, applying the training of OSA in the prevention of ecotoxicological impacts, the present study indicates the main regions in which priority actions should occur in case of oil spill in the São Paulo river estuary: the lower estuary, in the vicinity of the P2 and P4 stations, the middle estuary region at the stations P7, P8, and P10, and at the upper estuary specifically at the P18 station (Fig. 5b), since through the simulation results, these regions showed higher concentrations of OSA with negative buoyancy, which will reach the sensitive organisms (Moreira et al. 2015; Miranda et al. 2016; Rios et al. 2017).

In addition, the concentrations of PAHs dispersed by the OSA to the bottom of the simulation units (negative buoyancy) were compared with the limits of the ERL (effects range low) and ERM (effects range medium) indices were compared to know what the regions would have extensive impacts on benthic organisms (Fig. 6).

The ERL values for the sum of PAHs are 4.02 ng g^{-1} and ERM 44.79 ng g^{-1}. Concentrations below the ERL indicate that the biological effect tends to be rare. If concentrations are equal to or greater than ERL, but below ERM, this indicates that a biological effect will occasionally occur. Concentrations with or above ERM indicate that a negative biological effect will occur frequently (Buchman 2008). Analyzing Fig. 6, it will be noticed that ecotoxicological effects will occur in almost all the simulation units, except for stations P2 and P6.

The simulations showed that PAHs at the bottom of the simulation units would cause negative effects on benthic species, which over time could interrupt the development of these communities (Santos 2014). The ecological implications would be mainly emergence of anomalies, decreased fertility, and disappearance of fauna and flora (Nisbet and Lagoy 1992; Baumard et al. 1998; Peters et al. 1999; Savinov et al. 2003).

Although the formation of OSA reduces surface oil concentrations by transferring to the water column where there will be greater biodegradation, impacts to pelagic organisms, albeit to a lesser extent, should not be ignored. Some authors argue that hydrocarbons dispersed by suspended particles have a neutral effect on zooplankton (Conover 1971; Mackie et al. 1978); however, the contaminant can be biomagnified by larger fish (Wells and Percy 1985). In this sense, in the worst-case scenario, not occurring biodegradation in the water column of the dispersed PAHs, all simulation units representing the points of the São Paulo river estuary would present ecotoxicological risks to pelagic species; however, these effects would be reduced due to the natural biodegradation of these compounds (Lee et al. 1996; Fitzpatrick et al. 2015).

When there is an oil industry accident, the impacts are inevitable, and in this sense, the understanding of the formation of the OSA and its application is intended to mitigate these impacts and guide mitigation actions, making it clear that there are limitations of this method; however, given the greater impact of the accident, through OSAs, such damages are or can be reduced through biodegradation in the water column and indication of areas where biodegradation will hardly occur.

Conclusions

The formation of material oil aggregate in the São Paulo river estuary was efficient in the dispersion of polycyclic aromatic hydrocarbons added to the simulation units. The values of dispersed PAHs in this study exceeded the expectations in some simulation units. These results are useful for studies of oil dispersion in an estuarine environment and contribute to the framework of data generated by previous works, as well as providing unprecedented data on dispersion of polycyclic aromatic hydrocarbons as a function of aggregate formation in oil-suspended particulate material.

The OSAs formed during the experiments acquired neutral buoyancy in most simulation units, dispersing the PAHs into the water column. There was greater dispersion of low molecular weight PAHs. The main characteristics of the estuary that correlated with the formation of OSAs were salinity (negative) and chlorophyll *a* (positive) concentration.

In an oil spill scenario, according to what was studied, benthic and nectonic species would suffer ecotoxicological impact. The results found in this study are the result of an oil spill simulation experiment. The simulation units represented the São Paulo river estuary. The main characteristics of the surface waters were maintained; however, the experiment was carried out in the laboratory, and in the real estuarine environment, there may be some variations due to their dynamicity.

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