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Assessing legacy contaminants in sediments from marine protected areas of the central coast of São Paulo (Brazil)*

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ABSTRACT

The presence of legacy contaminants in sediments from three Marine Protected Areas (MPAs) of the coast of São Paulo State was evaluated. Four sampling surveys were conducted between 2013 and 2015 in 10 sites, distributed along the Laje de Santos Marine and Xixova-Japui State Parks (PEMLS and XJSP, respectively) and Central Coast Marine Protection Area (APAMLC). Samples were analyzed for sediment texture, total organic carbon, CaCO3, metals (Al, Fe, Hg, Cd, Co, Cr, Cu, Ni, Pb and Zn), aliphatic and polycyclic aromatic hydrocarbons (AH and PAH). Sediments were generally sandy (excepting muddy samples from APAMLC), with variable amounts of TOC, OM and CaCO3. Most of the sediments exhibited low to moderate concentrations of metals, except APAMLC. Low contamination of sediments by hydrocarbons was found but samples from XLSP and APAMLC exhibited the highest concentrations of biogenic AH and PAH from pyrogenic sources. In APAMLC and PEMLS, the levels of metals can be considered as background levels according to geochemical indices (Igeo and EF). In XJSP and especially in APAMLC data indicated poor sediment quality, probably due to the effect of anthropic activities.

Descriptors: Environmental Monitoring, Geochemistry, Metals, Organic Compounds, Sediment Contamination, Marine Pollution.

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RESUMO

A contaminação dos sedimentos superficiais foi avaliada neste estudo em amostras de áreas marinhas protegidas (AMP) da costa central de São Paulo. Quatro campanhas de amostragem foram feitas entre 2013 e 2015 em 10 sítios localizados nos Parques Estaduais Marinho da Laje de Santos e Xixová-Japuí (PEMLS e PEXJ, respectivamente), e Área de Proteção Ambiental Litoral Centro (APAMLC). As amostras foram analisadas quanto granulometria, carbono orgânico total, CaCO3, metais (Al, Fe, Hg, Cd, Co, Cr, Cu, Ni, Pb e Zn) e hidrocarbonetos alifáticos(AHs) e policíclicos aromáticos (PAHs). Em geral os sedimentos foram arenosos (exceto aqueles de APAMLC, que foram lamosos) e com quantidades variáveis de COT, MO e CaCO3. A maioria das amostras apresentaram baixas concentrações de metais de acordo com índices geoquímicos (Igeo e fatores de enriquecimento - FE). Baixa contaminação por hidrocarbonetos foi encontrada e em APAMLC os sedimentos apresentaram as maiores concentrações de AHs de origem biogênica e PAHs de pirogênicos. Nos sedimentos de APAMLC e PEMLS, os níveis de metais podem ser considerados como valores de referência. Já em PEXJ, os dados indicaram baixa qualidade de sedimentos, possivelmente devido às fontes antrópicas.

Descritores: Monitoramento Ambiental, Geoquímica, Metais, Compostos Orgânicos, Contaminação dos Sedimentos, Poluição Marinha.

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INTRODUCTION

Marine Protected Areas (MPAs) are considered "any area of intertidal or subtidal terrain, together with its overlying water and associated flora, fauna, historical and cultural features, which has been reserved by law or other effective means to protect part or all of the enclosed environment" (KELLEHER et al., 1995). These areas have been established all over the world, for the purposes of protecting fish stocks, exporting biomass to surrounding regions (spill-over) and preserving particular species, ecological processes and landscapes, among others.

The proper planning and management of MPAs rely on a set of actions and policies that must be implemented in order to ensure effective protection of the marine ecosystems. However, recently POZO et al. (2009) and TERLIZZI et al.(2004) have stated that MPAs located close to human activities are influenced by chemicals originating outside them, and recent literature has correlated the presence of contaminants within MPAs with negative effects on the biota (DAVANSO et al., 2013; RODRIGUES et al., 2013, CRUZ et al., 2014; GUSSO-CHOUERI et al., 2015; NILIN et al., 2013). Thus, for an effective MPA management it is important to determine the pollution status of the area, which can be achieved by monitoring the concentrations of chemical substances in the environmental compartments. Assessments of environmental quality status have frequently consisted of monitoring the chemicals in the sediments (CHAPMAN, 2002). Many contaminants precipitate directly onto the bottom substrates; others adsorb onto the suspended particles and sink to the bottom, accumulating thus in such deposits (INGERSOLL, 1995).

The central coast of the State of São Paulo includes a series of MPAs, which are part of the mosaic of marine and coastal protected areas of São Paulo (SÃO PAULO, 2008a); such list includes the Laje de Santos Marine State Park (PEMLS), the Xixova-Japuí State Park (XJSP) and the Central Shore Marine Protected Area (whose local acronym is APAMLC). However, this region is also affected by multiple pollution sources (ABESSA et al., 2008; LAMPARELLI et al., 2001). Inputs of contaminants into the metropolitan region of the Baixada Santista include large-scale discharges of sewage and industrial effluents, littering, and the release of contaminants in the Port of Santos. Besides, large cargo ships use the proximities of local MPAs as anchoring sites and constitute thus a potential source of pollutants (THOMAS et al., 2002; THOMAS et al., 2000). The disposal site of sediments dredged from the Port of Santos near the MPAs, also constitutes another potential source of contamination.

Considering the scenario of XJSP, APAMLC and PEMLS potentially affected by contamination, it is necessary to assess the presence and concentrations of chemical substances in the sediments in order to establish reference values as baseline concentrations and thus provide information for the management of these MPAs. The present investigation aimed to monitor the sediment quality in three MPAs located on the central coast of São Paulo (XJSP, PEMLS and APAMLC) by measuring the concentrations legacy contaminants including metals and hydrocarbons in samples collected in different periods between 2013 and 2015.

MATERIAL AND METHODS

Study Area

This investigation covers a broad area of the central coast of São Paulo, involving 6 sampling sites within the PEMLS (P5 to P10), one site in the XJSP (P1), two sites in the APAMLC (P2 and P3) and one at the disposal site of dredged material from Port of Santos (P4) in the vicinity of each of these MPAs (Figure 1; Table 1). The PEMLS was created in 1993 and was the first marine park in the State. It is located within the Itaguaçu sector of the APAMLC. This park aims to protect the marine ecosystems of the southwestern Atlantic coast (SÃO PAULO, 1993), and is considered a priority area for marine conservation (BRASIL, 2002). The oceanographic regime alternates the presence of warm coastal waters and cold and nutrient-rich waters from upwelling; a situation which favors the development of an abundant and diverse marine life (LUIZ-JUNIOR et al., 2008).

The APAMLC presents three sectors (SÃO PAULO, 2008b): Guaíbe, in the northeast; Itaguaçu, in the south and surrounding the PEMLS, and Carijó, in the southwest. Few studies on this MPA have focused on environmental pollution (CESAR et al., 2014; TORRES et al., 2009; SOUSA et al., 2007); they did agree, however, in attributing poor quality to the sediments close to Moela Island and northeastwards due to influence of dredged sediments disposal and port activities.

The XJSP is a coastal protected area that presents a marine portion of 301 ha. There is evidence that contaminants from various sources tend to be transported towards this area by coastal currents (LAMPARELLI et al., 2001; ABESSA et al., 2008b; SÃO PAULO, 2010). Previous data for this MPA detected toxicity for both surface and bottom water samples and sediments (SÃO PAULO, 2010), sediment contamination (LAMPARELLI et al., 2001; MARTINS et al., 2008; ABESSA et al. 2008; CAMARGO et al., 2015; ARAUJO et al., 2013) and consequent negative effects on metabolism and physiology of bivalves (PEREIRA et al., 2011; 2012).

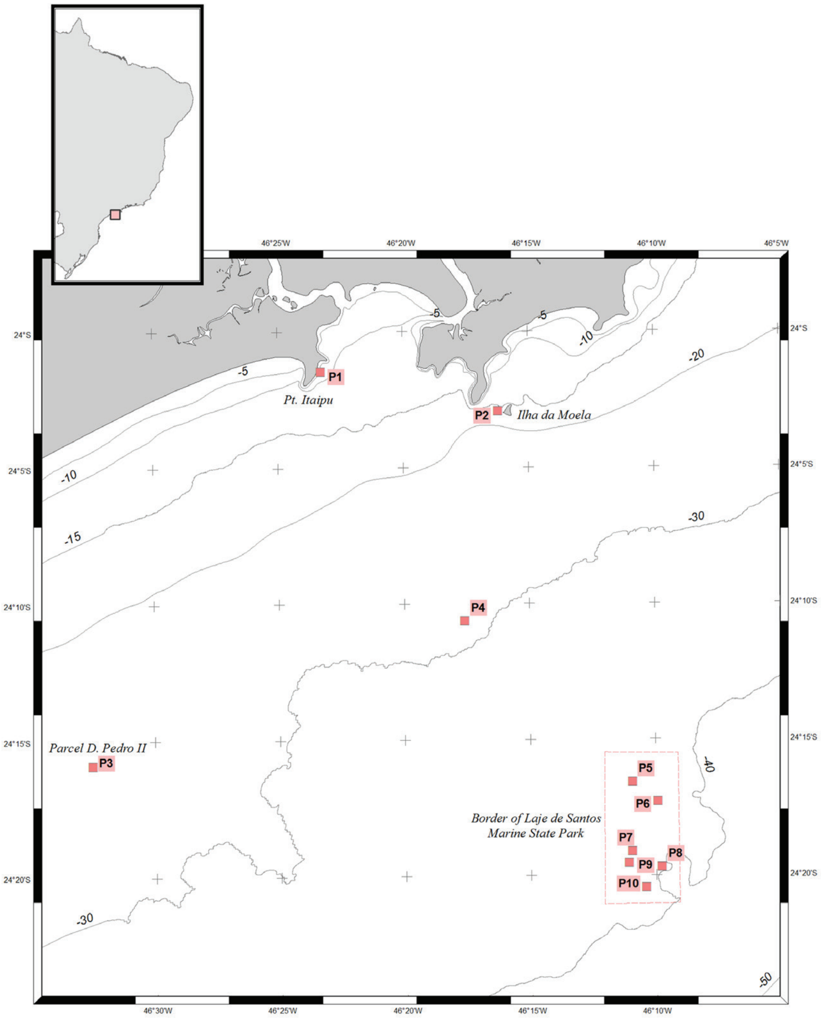

Figure 1. Map of the areas studied showing the sampling sites of sediments.

SEDIMENT COLLECTION

Four surveys were conducted for sampling sediments between 2013 and 2015. The first survey consisted of collections made on September 3rd, 2013, October 14th, 15th and 17th, 2013. The second survey was conducted between January 29th and 31st, 2014. The third survey occurred between July 1st and 3rd, 2014; and the fourth survey was undertaken on January 20th, 21st and 26st, 2015 (totaling 40 samples).

Sediments were collected by using a van Veen grab sampler with 0.06 m^2 covering the top 5cm layer. The material retained in the sampler was thoroughly homogenized, and aliquots were separated for the analysis of grain size, total organic carbon (TOC), calcium carbonate ($CaCO_3$), metals and hydrocarbons. Samples for sediment properties and metals determinations were transferred to laboratory in plastic containers and kept at 4ºC until the analyses, while those for organic chemicals were kept in metal foil recipients at -20 ºC.

SEDIMENT CHARACTERISTICS

The analysis of physical properties of the sediment samples were performed by the SALT - Sea & Limno Technology Ltd (SALT Ambiental). Grain size distribution was measured in HCl-decarbonated samples by the wet-dry sieving method followed by pipette to method for clays and silts (MUDROCH; MACKNIGHT, 1994). The analysis of $CaCO_3$ was conducted by HCl digestion (decarbonization) and gravimetry (GRANT-GROSS, 1971). Decarbonated sediments were separated for total organic carbon estimation (TOC) in accordance with the method of oxidation with potassium dichromate described by GAUDETTE et al. (1974).

LEGACY CONTAMINANT ANALYSES

Determination of major (Al and Fe) and trace metals (Hg, Cd, Co, Cr, Cu, Ni, Pb and Zn) concentrations were performed in samples digested with an acid solution containing 9 mL of HNO_3 and 3 mL of HCl, according to the EPA 3051A protocol (USEPA, 2007) in a high pressure microwave system (CEM Corporation, model MDS—2000). Concentrations of Pb and Ni were measured in the extracts using the flame mode of a Fast-Sequential Atomic Absorption Spectroscope Varian (model Spectr-AAS-220-FS) with a deuterium lamp background correction. Levels of Hg were measured by cold vapor generation with the spectrometer coupled to a typical FIA (Flow Analysis Injection) manifold, with a manual injection valve that injects 500 µL of sample at a flow of Milli-Q water (10 mL min-1). The validation of this method was performed by the analysis of two Standard Reference Materials (SRM 2704 - Buffalo River Sediment and SRM-1646a - Estuarine sediments), in three replicates. Details of these analyses are shown in the (Appendix 1). available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing).

For hydrocarbon analyses sediment samples were freeze-dried and homogenized. An amount of 20g was Soxhlet-extracted with a 50% mixture of n-hexane and dichloromethane for 8 hours, in accordance with UNEP (1992). The hydrocarbon extracts were fractionated into F1 (aliphatic hydrocarbons - AHs) and F2 (PAHs) by silica gel-alumina column chromatography. Twenty-six aliphatic hydrocarbons (n-C17 to n-C35, including pristane and phytane) were determined on a gas chromatography 6890 from Agilent Technologies with a flame ionization detector (GC-FID) and a capillary fused silica column coated with 5% diphenyl/dimethylsiloxane (30 m x 0.25 mm ID and 0.25 µm) using hydrogen as the carrier gas. Thirty-three PAHs were analyzed by an Agilent 6890 gas chromatograph coupled to a 5973N mass spectrometer (GC/MS) in a selected ion mode (SIM) with a similar column used in AHs using helium as the carrier gas. The oven temperature for AHs and PAHs was set from 40 ºC for 2 min, raised to 40–60 ºC (at 20 ºC min^{-1}), then to 290 ºC (at 5 ºC min^{-1}) held for 5 min, and finally to 300 ºC (at 10 ºC min^{-1}) held for 10 min.

Individual compounds were identified by matching their respective retention time with standards confirmed by matching their ion mass. Quantification was performed by the surrogate peaks area method and a 5-point calibration curve for each group of compounds ($r > 0.995$). Quality assurance and quality control (QA/QC) were based on the analysis of blanks, matrix spike, matrix duplicate and standard reference material. The mean recoveries of surrogates and target compounds were within 65 and 102%. The precision ranged from 1.8 to 12% for AHs, and from 1.6 to 19% for PAHs. The method's accuracy was ensured by the analyses of standard reference material from the International Atomic Energy Agency (IAEA 417). The method detection limit (MDL) was based on the standard deviation (3xσ) of seven replicates of a sediment sample containing target compounds (Appendix 2). available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing).

DATA ANALYSIS AND INTERPRETATION

Two indices were applied to classify the quality of samples based on the concentrations of metals. The first one was the index of geo-accumulation (I_{geo}) that has been defined by MULLER (1979) as a criterion to evaluate the metal pollution. Given the parameters, C*n* refers to the sedimentary concentration of a particular metal, *n*, measured; B*n* represents the baseline value or reference site for the metal *n*; and the 1.5 factor corresponds to variations due to lithological processes. The I_{geo} for each sample was calculated using the following model:

$$I_{geo} = \log2 (Cn/1.5* Bn)$$

Then, I_{geo} results are applied to a qualitative scale of contamination intensity (Appendix 3) available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1x

ACJaGm50z12Dzja?usp=sharing). and according to this scale, samples with I_{geo} above 1 show early signs of contamination. In our study, sediment samples were classified in accordance with the worst ranking of contamination presented for each element, i.e., if the sample showed enrichment by a single element, it was ranked on the basis of this worst condition (BURUAEM et al., 2012).

We also applied the normalization followed by the calculations of the enrichment factors (EF). Such approach has been widely used to detect anomalous concentrations of metals in sediments considering effects from different aspects such as grain size, correction with inert mineral, comparison with conservative elements and background levels (ALOUPI; ANGELIDIS, 2001; ADAMO et al., 2005; HORTELLANI et al., 2008). In this study, the enrichment factor (EF) for each element based on reference values were also calculated, as (1), where C_{sed} is the concentration of a given metal in each sample and C_{back} is the background or reference value. If the EF is higher than 1it can be considered an indicator of an anthropogenic source. The degree of pollution by computing a total enrichment factor (R) for each station was assessed by averaging the EF values of all metals. Samples with values below the quantification limit (QL) were calculated using their own QL value. Using these calculations, a classification of the sites examined was made in accordance with the criteria: highly contaminated (R > 3), moderately contaminated (2.0 < R < 3.0), weakly contaminated (1.0< R < 2.0) and uncontaminated (R<1) (ADAMO et al., 2005).

$$EF= (C_{sed}-C_{back})/C_{back} \quad (1)$$

$$R= (\sum EF)/n \quad (2)$$

For both indices, due to the lack of studies focusing on the geochemical background of metals for the particular sector of MPAs, baseline levels were calculated using the mean values of concentrations obtained by HOFF et al. (2015) for the Alcatrazes Archipelago (São Sebastião) and Palmas and Cabras islands (Ubatuba), two sets of islands that are part of a highly restricted MPA. For Co, we used the baseline value proposed by LUIZ-SILVA et al. (2006) for the Santos Estuarine System.

Different diagnostic indices were applied in order to identify the main sources of hydrocarbons (Appendix 4). available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing). Threshold values proposed by BAUMARD et al. (1998) and applied for he analysis of similar set of PAHs in samples from Mediterranean Coastal (BARAKAT et al., 2011) were used to classify the sediment samples into 4 status of contamination as low, moderate, high and very high when ∑PAHs concentrations are 0–100, 100–1000, 1000–5000 and > 5000 ng/g, respectively.

RESULTS

The results of the sediment properties analysis are presented in table 1 including TOC, $CaCO_3$ and mud. Sediment samples were predominantly sandy in all the surveys, as can be observed from the low mud content, except at P2 which presented values between 90 and 100% of mud. Levels of TOC were low ranging from 0.07 to 0.48%. Samples from P2 also presented higher levels of OM and TOC in all the surveys (except for the first survey).

Table 1. Sediment properties of samples from the MPAs of the Central Coast of São Paulo. Total Organic Carbon (TOC), $CaCO_3$ and Mud are expressed in %.

Survey		**Depth (m)**	**TOC (%)**			**$CaCO_3$ (%)**				**Mud(%)**				
		S1	**S2**	**S3**	**S4**	**S1**	**S2**	**S3**	**S4**	**S1**	**S1**	**S2**	**S3**	**S4**
Sampling sites	P1	9	0.18	0.32	0.07	0.58	2.33	2.41	3.92	6.42	0.06	0.84	3.69	14.64
	P2	20	0.36	3.68	2.59	1.96	7.70	8.71	12.11	13.49	100.00	100.00	97.12	91.20
	P3	25	0.31	0.18	0.22	0.13	85.13	2.14	83.42	3.07	2.82	0.19	3.36	3.17
	P4	20	0.22	0.19	0.07	0.12	3.28	3.10	4.06	3.68	0.30	0.26	0.38	2.49
	P5	35	0.29	0.14	0.21	0.00	26.97	8.94	5.45	5.44	0.72	0.41	0.74	3.56
	P6	15	0.31	0.22	0.21	0.21	6.55	2.50	2.6	78.80	0.62	0.57	1.20	24.93
	P7	30	0.49	0.49	0.20	0.28	58.07	77.64	78.5	80.07	2.51	4.16	2.79	11.03
	P8	35	0.48	0.23	0.37	0.16	61.95	5.06	67.98	5.14	3.7	0.21	17.12	6.12
	P9	20	0.48	0.41	0.29	0.24	68.04	92.93	64.49	88.66	6.71	6.22	27.14	31.23
	P10	35	0.31	0.19	0.11	0.24	7.07	2.56	4.85	27.06	0.74	0.86	1.44	7.25

Major and trace elements contents are presented in Figure 2. In general, the results showed low concentrations of metals. Concentrations of Cd were below the detection limits in all the samples from all the surveys. The highest concentrations of Al, Fe, Cr, Co, and Zn were found near the coastal area (P1 and P2) in all the surveys and these data can be attributed to the terrigenous contribution and anthropic influence. The trace elements Cu, Pb, Ni and Hg presented high concentrations at P2.

The results of I_{geo} and EF are shown in Table 2. For I_{geo}, samples from P3 to P10 were often classified as background values and P1 was classified as uncontaminated in the first, second and fourth surveys. Samples from P2 were considered as "uncontaminated to moderately contaminated" (third survey) and "moderately contaminated" (first, second and fourth surveys). The EF showed a similar pattern, with EF values indicating P3 to P10 as uncontaminated in all surveys, except P10 in the second survey which was classified as weakly contaminated. Samples from P1 were classified as uncontaminated in the third survey, weakly contaminated (first and second surveys) and moderately contaminated (fourth survey). Samples from P2 were considered as highly contaminated in all the campaigns.

Results of aliphatic hydrocarbons (AHs) including n-alkanes (from C12 to C35), unresolved complex mixture (UCM), carbon preference index (CPI) and dominant peaks are presented in Figure 3 and in Appendix 5. available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing). The AH concentrations in the samples of all the surveys were often low, ranging from 0.55 to 4.84 µg.g^{-1} at P1 and P3 to P10, while the concentrations at P2 were higher and ranged from 21.2 to 39.1 µg.g^{-1}. Total concentrations and Polycyclic Aromatic Hydrocarbons (PAHs) are presented in Figure 3 and Appendix 6. available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing). No PAHs were detected in 16 of the 40 samples from P4, P5 and P6 (in the first, second and third surveys) and P10 in the first and third surveys. The concentrations detected at P1, P3, P7 P9 and P10 ranged from 1.55 to 132 ng.g^{-1}. The interpretation of diagnostic ratios of AHs and PAHs sources are presented in discussion section.

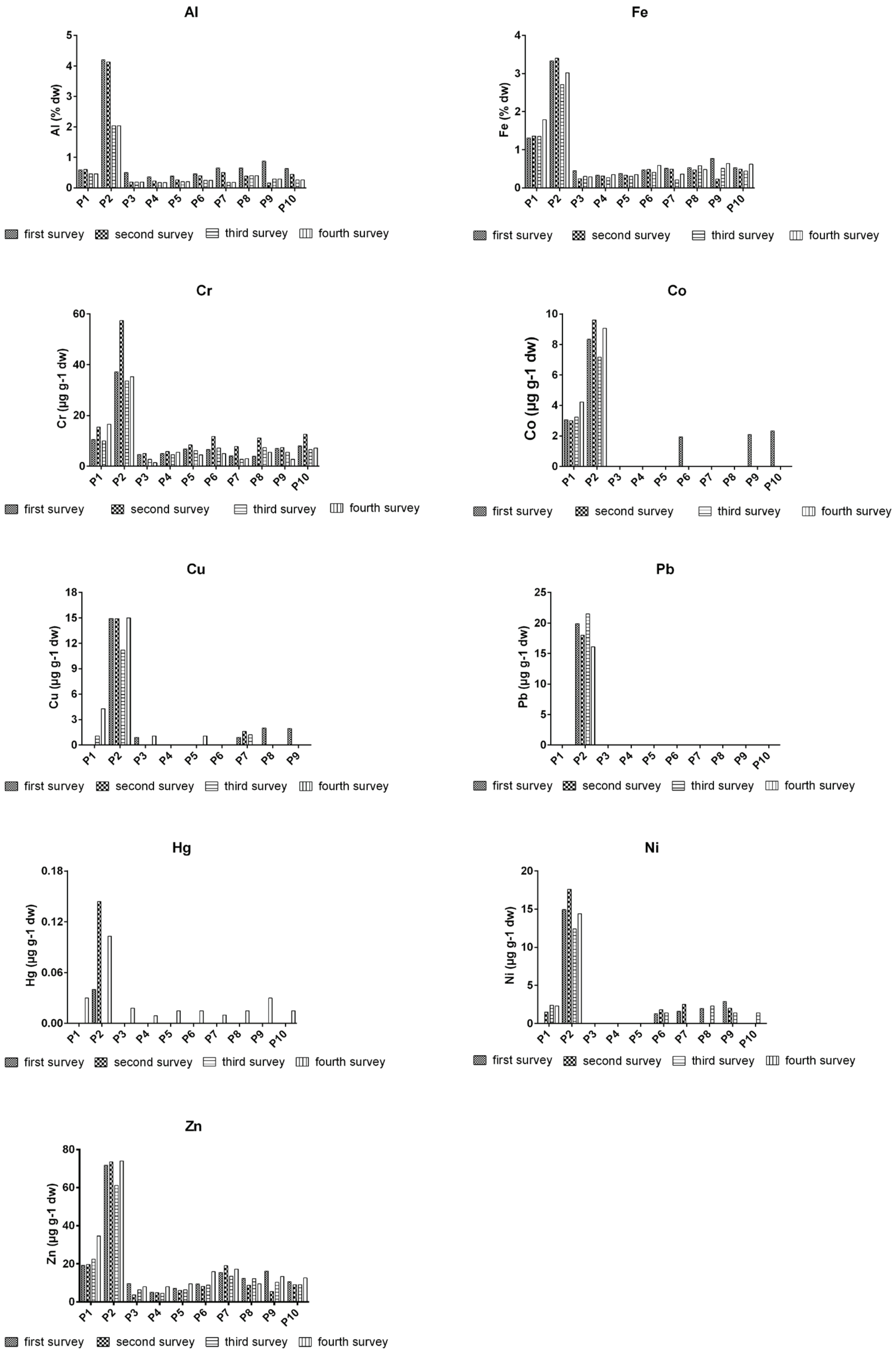

Figure 2 – Spatial distribution of major and trace metals in sediments from MPAs located on the Central coast of São Paulo, during the four surveys (2013 - 2015).

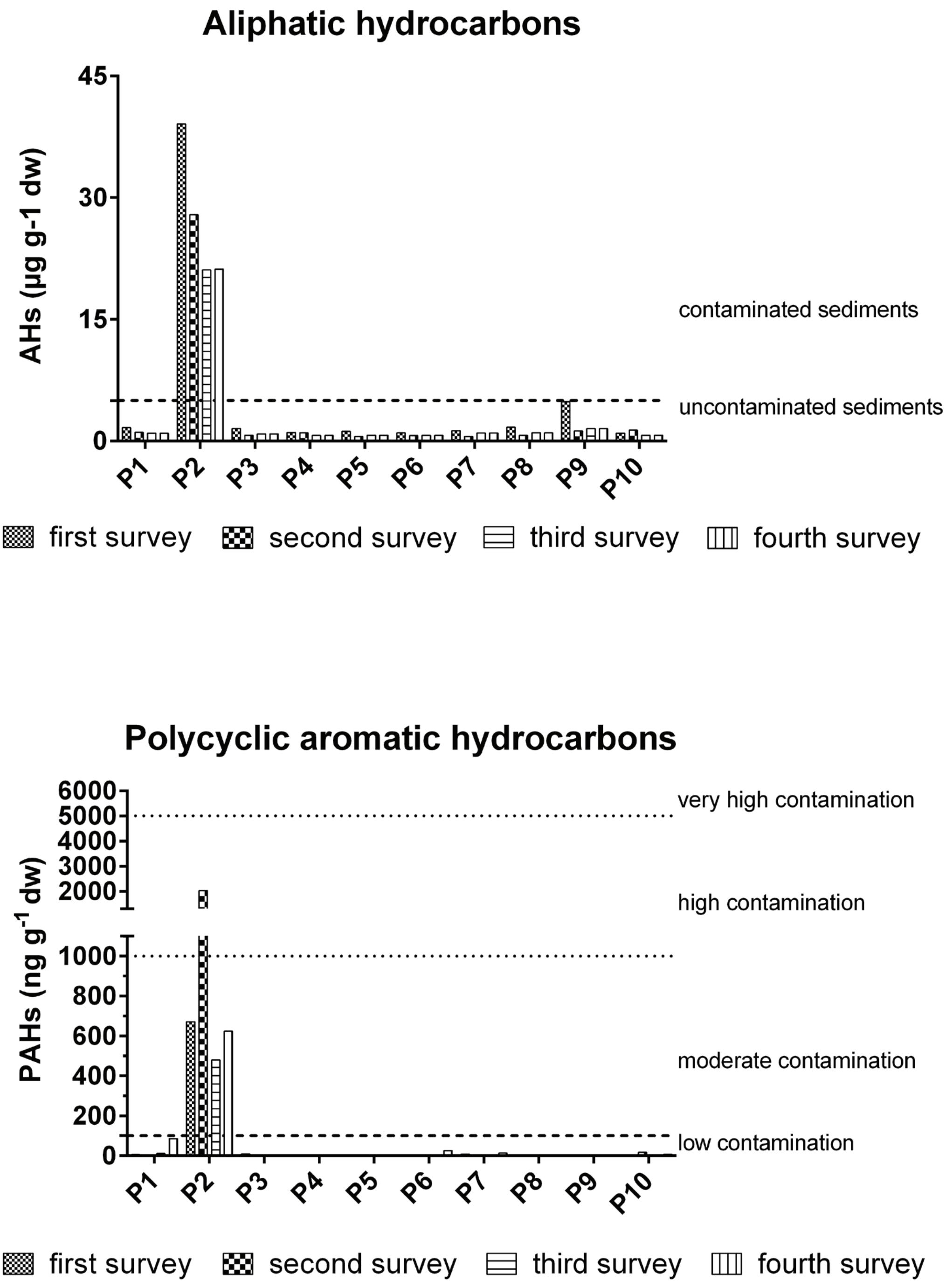

Figure 3. Spatial distribution of aliphatic and polycyclic aromatic hydrocarbons in sediments from MPAs located on the Central coast of São Paulo, during the fourth survey (2013 - 2015).

Table 2. Comparison of qualitative classification of sediments based on different interpretative approaches

Samples Index		I_{geo}			**EF**
		Classification	**Index**	**Classification**	
First survey	P1	0.15	Uncontaminated	1.02	**Weakly contaminated**
	P2	2.08	**Moderately contaminated**	7.35	**Highly contaminated**
	P3	-0.33	Background levels	0.11	uncontaminated
	P4	-0.53	Background levels	-0.08	uncontaminated
	P5	-0.25	Background levels	0.13	uncontaminated
	P6	-0.72	Background levels	0.19	uncontaminated
	P7	-0.33	Background levels	0.41	uncontaminated
	P8	-0.14	Background levels	0.54	uncontaminated
	P9	-0.12	Background levels	0.84	uncontaminated
	P10	-0.32	Background levels	0.35	uncontaminated
Second survey	P1	0.27	Uncontaminated	1.31	**Weakly contaminated**
	P2	2.44	**Moderately contaminated**	9.20	**Highly contaminated**
	P3	-0.90	Background levels	-0.13	uncontaminated
	P4	-0.68	Background levels	0.04	uncontaminated
	P5	-0.40	Background levels	0.34	uncontaminated
	P6	-0.20	Background levels	0.67	uncontaminated
	P7	0.05	Uncontaminated	0.71	uncontaminated
	P8	0.02	Uncontaminated	0.87	uncontaminated
	P9	-0.71	Background levels	0.02	uncontaminated
	P10	-0.10	Background levels	1.06	**Weakly contaminated**
Third survey	P1	-0.10	Background levels	0.96	uncontaminated
	P2	1.89	**Uncontaminated to moderately contaminated**	6.00	**Highly contaminated**
	P3	-0.89	Background levels	-0.20	uncontaminated
	P4	-0.88	Background levels	-0.14	uncontaminated
	P5	-0.64	Background levels	0.09	uncontaminated
	P6	-0.58	Background levels	0.21	uncontaminated
	P7	-0.65	Background levels	-0.07	uncontaminated
	P8	-0.23	Background levels	0.59	uncontaminated
	P9	-0.38	Background levels	0.23	uncontaminated
	P10	-0.41	Background levels	0.20	uncontaminated
Fourth survey	P1	0.72	Uncontaminated	2.62	**Moderately contaminated**
	P2	2.21	**Moderately contaminated**	7.66	**Highly contaminated**
	P3	-0.68	Background levels	-0.01	uncontaminated
	P4	-0.53	Background levels	0.17	uncontaminated
	P5	-0.40	Background levels	0.17	uncontaminated
	P6	-0.08	Background levels	0.78	uncontaminated
	P7	-0.39	Background levels	0.31	uncontaminated
	P8	-0.26	Background levels	0.49	uncontaminated
	P9	-0.07	Background levels	0.89	uncontaminated
	P10	-0.06	Background levels	0.82	uncontaminate

DISCUSSION

The analyses of sediment properties indicate the local hydrodynamic characteristics, especially at P2, where the deposition of fine particles is the result of low hydrodynamic energy. Thus, the results are consistent with the expected pattern for the region. Sand and gravel accounts for more than 50% of the surface sediments from the inner shelf and an increase on the outer shelf of between 28° and 36°S, while silts and clays are predominant between the 50 and 100m isobaths on the middle shelf (MAHIQUES et al., 2004; NAGAI et al., 2014).

Levels of OM corroborate the occurrence of a depositional zone at P2 and regarding $CaCO_3$, the results varied considerably between surveys and sampling sites, with higher levels were found at P7 and P9, in all the surveys, and at P3 and P8 in the first and second surveys. The variation in the data indicates the contribution of different sources and transport of OM and bioclastic materials (autochthonous or allochthonous) that may have originated from coralline algae, barnacles, mollusks or amounts of agglutinated Foraminifera (MILLIMAN,1993).

Major and trace metals occur in natural levels and the identification of anomalous concentrations linked to contamination is difficult and direct measurements of environmental concentrations may not reflect anthropogenic sources (SCHIFF; WEISBERG, 1999). To deal with this, a proper identification of anthropogenic influences can be estimated through baseline concentrations (SINGH et al., 2003). Such levels reflect a specific concentration in a particular period of time that may not reproduce the true background but in areas without intense or direct anthropogenic influences, the baseline may, however, reflect the background levels (SINGH et al., 2003) and they can be considered as constituting the interval that comprises at least 90% of all observations (KABATA-PENDIAS et al., 1992).

As mentioned, due to the lack of data on the background of metals for each particular sector of the three MPAs studied, baseline concentrations were proposed for each element based on the percentile distribution and the interval between 5% and 95% of the data, with the exception of P2 which was excluded from the analysis because this site was considered contaminated. These baseline ranges are presented in Table 3 along with the concentration of metals in superficial sediments from some coastal environments of the Southeast and South regions in Brazil. The concentrations of metals in the MPAs located on the Central Coast of São Paulo are low compared with those obtained for the estuarine systems of Paranaguá (PR), Santos - São Vicente (SP) and Vitória (ES). This situation was expected since estuarine environments are more influenced by terrigenous inputs than are marine environments, including the inner shelf, and also because estuaries are often impacted by anthropic contamination. However, the baseline levels are similar to (or slightly higher than) the concentrations obtained for the superficial sediments of the Tupinambás Ecological Station (HOFF et al., 2015), an MPA located on the Northern coast of São Paulo which presents similar characteristics of sediment type to those found in the PEMLS and at P3.

Low concentrations of AHs were detected in sediment samples with the higher levels observed at P2 in all the surveys. Related to such distribution, levels of total n-alkanes ranged from 0.01 to 1.36 µg g^{-1} at P1 and P3 to P10 while higher values, from 5.04 to 10.3, were found at P2. According to VOLKMAN et al. (1992), concentrations of n-alkanes above 50 µg g^{-1} can be related to polluted samples and concentrations below 10 µg g^{-1} are normally due to biogenic sources and unpolluted sediments. Based on this, the results of AH analysis suggest a natural input of these hydrocarbons for most of the samples, except for P2 in the first survey. READMAN et al. (2002) suggest that samples with concentrations below 50 µg g^{-1} require the use of different markers for a better discrimination between biogenic and anthropogenic contributions.

The Carbon Preference Index (CPI) was calculated from the analysis of the n-alkanes. The CPI assesses the odd-to-even hydrocarbon predominance in compounds with more than 25 carbons (ABOUL-KASSIM; SIMONEIT, 1996). Such description is important for the characterization of sources as the contribution of terrestrial plant waxes (CPI between 4 and 7) and the petroleum contribution (CPI generally gives a value of around 1.0) (NRC, 1985, WANG et al., 1999). CPI values were not calculated for most samples due to low levels of AHs found below the limit of detection (LD). For those whose CPI were calculated such P9 (the second survey) the result suggests an oil source, but again, this contribution is not relevant due to low levels found for n-alkanes. More important results were found in samples from P2 (in all surveys), P1 (the fourth survey) and P9 (the first survey) which presented CPI values indicating a biogenic contribution.

The isoprenoid alkanespristane (Pr) and phytane (Ph) are formed by the transformation of phytol and other natural products into petroleum and they are also present in petroleum samples (TAMEESH; HANNA, 1986). Pristane can also be produced by zooplankton whereas phytane is associated with Archaebacteria and can be abundant in anaerobic sediments (VOLKMAN et al., 1992). Thus, the ratio pristane/phytane (Pr/Ph) is used as indicative of petroleum contamination, where ratios between 3 and 5 are related to uncontaminated sediments, as compared to contaminated sediments and crude oil samples, which tend to present low Pr/Ph ratios (TAMEESH; HANNA, 1986). It was not possible to calculate the Pr/Ph ratios for most of the samples due to the absence of one or both compounds. Pr/Ph ratios related to crude oil samples were found only at P1 and P3 in the first survey and P9 in the second survey but as observed for CPI, this contribution is not relevant.

Another marker of hydrocarbons derived from oil is the presence of unresolved complex mixture (UCM), defined as a raised baseline hump that is often observed in petroleum gas chromatograms. Such signals are related to the majority of molecules present in the total aliphatic hydrocarbons that cannot be resolved by capillary GC columns and it is a common characteristic of biodegraded oil chromatograms and can be used as an indicator of oil pollution (VOLKMAN et al. 1992). Only samples from P2 presented detectable concentrations of UCM and they accounted for more than 50% of AHs, indicating the occurrence of oil hydrocarbons in those samples.

PAHs are normally present in oil and its derivatives and they can also be released from natural sources such as biomass combustion, volcanic eruptions and diagenesis (LAW; BISCAYA, 1994). Anthropogenic sources include the burning of coal and wood, diesel and oil combustion, industrial activities, effluents and accidental fuel spills (TOBISZEWSKI; NAMIESNIK, 2012). These samples can be classified as uncontaminated in accordance with the classification proposed by BAUMARD et al. (1998a). On the other hand, samples from P2 presented values of between 480 and 2023 ng.g^{-1} and these levels can be considered indicative of moderate contamination (first, third and fourth surveys) and high contamination (second survey).

Low molecular weight PAHs (LMW) include petrogenic hydrocarbons originating from unburnt PAHs or those burnt at low temperatures such as crude oil and refined products whereas the high molecular weight PAHs (HMW) represent pyrogenic compounds, which are derived from combustion sources, such as vehicle exhaust fumes and coal and forest fires (BAI et al. 2014; ÜNLÜ et al. 2010). The ratios of ∑LMW/∑HMW >1 suggests the contribution of petrogenic input of PAHs in sediments from P3, P8 and P9 (first survey), P7 (second survey), P6, P7 and P9 (fourth survey). Pyrogenic sources were identified at P1 (fourth survey) and P2 (all surveys), indicating the influence of land-based activities. These results might indicate inputs from nautical activities such as ships anchored in the vicinity, pleasure and/or fishing boats and dredging of sediments.

Diagnostic ratios for the identification of PAH sources were calculated only for P1, P2, P9 and P7 (Appendix 6) due to due to high number of samples below MDL. For those samples the ratios of Ant/∑178, BaA/∑228, Phe/Ant and Ind/∑276 ratios indicate a combustion source at P2 (all surveys) and PAHs from petroleum at P9 (first survey). Results of Fl/∑202 ratios indicated a contribution from grass, wood and coal combustion for these same samples. Due to contrasting results, we looked at perylene distribution (Per). Per is released into the atmosphere during the burning of fossil fuels, often being found in sediments (SILLIMAN et al., 1998). High levels of Per in the deeper layers of sediments indicate the deposition from anaerobic diagenesis of organic matter and low levels related to processing in the oxide zone (CAVALCANTE et al., 2009). Thus, levels of Per relative to the total PAH concentrations with five aromatic ring (%Per/∑PAHs 5 rings) >10% indicate a diagenetic processes (natural source) (BAUMARD et al., 1998b). By using such information, we can infer that the Per in samples from P1 (second, third and fourth and survey), P2 (first, third and fourth surveys) and P7 (third survey), presented contribution from natural origin. Same way as observed for AH the low concentrations found in P1, P7 and P9 indicate a low input of PAHs in these sites.

We performed Pearson's correlation coefficient analysis aiming to explore the distribution of contaminant (metals and hydrocarbons) associated with sediment properties (Appendix 7). available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing). Concentrations of Al, Zn, and PAHs were correlated positively with % mud. Such a pattern can be attributed to the results of P2 and P1 which are influenced by the deposition of materials from natural and anthropic origin that are transported along the coastal zone. In the region of P2, high levels of contaminants were previously reported indicating the environmental degradation in the region (TORRES et al., 2009; CESAR et al., 2014). The concentrations of TOC were correlated positively ($p<0.05$) to Zn, Ni, AL, Cu, Ah and PAHs. These results show that both fine particle sediments and TOC represent important geochemical carriers in MPAs of the coast of São Paulo State, regulating the distribution of these compounds (HEDGES et al., 1993; CHIOU et al., 1998).

Table 3. Distribution of major and trace metal distribution in different locations, including baseline values for the Marine Protected Areas located on the Central Coast of São Paulo. All values are expressed in µgg^{-1}, except Fe and AL which are expressed in %.

Location	Fe	AL	Hg	Cr	Co	Cu	Ni	Pb	Zn	author
Santos Estuarine System (SP)	0.26 - 7.99	0.06 -7.91	< 0.03 – 0.92	< 5.0 – 97.5	0.2-17	-	1.3-44.2	< 2.0-204.8	6.0-312.0	A
Vitoria Estuarine System (ES)	0.9 - 8.7	0.9 - 8.8	0.03-0.82	35 - 280	-	5-660	6-245	5-292	27-812	B
Paranaguá EstuarineSystem(PR)	-		-	14.50 - 58.00	-	<0.04-16.20	6.65-21.90	<0.30-29.75	26.95-80.50	C
Tupinambás Ecological Station (SP)	0.09 - 0,61	0.08 - 0.53	0.01-0.02	2.29 - 13.59	-	0.46-3.07	1.10-5.43	1.07-6.32	4.06-21.05	D
Baseline for MPAs of the Central Coast of SP	0.27 - 1.42	0.17 - 0.97	0.01 - 0.03	2.53 - 15.58	1.94 - 4.23	0.91 - 4.27	1.29 - 2.89	NC	4.41-24.31	E

A: Hortellani et al. (2008); B: Jesus et al.(2004); C: Choueri et al. (2009); D: Hoff et al. (2015); E: This Study.

In conclusion, sediments collected in MPAs of the Central Coast of São Paulo presented low contamination. The exceptions were samples from XJSP and APAMLC (P1 and P2, respectively), which presented enrichment of metals and high levels of hydrocarbons, probably due to their proximity to the coastal zone and the influence of anthropogenic activities. The results allowed the determination of the baseline and reference concentration for metals that were similar to levels found in other MPAs. The monitoring during the four surveys did not reveal any relevant variation on contaminant levels over the period. The results presented in this study are important diagnosis of the environmental status of sediments, which can assist the management of these MPAs.

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