# Assessing the sediment quality of the Laje de Santos marine state park and other marine protected areas of the central coast of São Paulo (Brazil)*

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## Abstract

In this study, the quality of sediments from three Marine Protected Areas (MPAs) located on the coast of São Paulo (Laje de Santos Marine State Park - PEMLS; Xixova-Japui State Park - XJSP; and Central Coast Marine Protection Area - APAMLC) was assessed. Four sampling surveys were conducted (September/October 2013; January 2014; July 2014; January 2015). Sediment samples were collected at10 sites, distributed along the 3 MPAs. Samples were analyzed for sediment texture, total organic carbon, $CaCO_3$, metals, aliphatic and polycyclic aromatic hydrocarbons, and for whole-sediment and sediment-water interface toxicities. Principal component analysis (PCA) was used to integrate data. Most of the sediments exhibited low concentrations of chemicals, with the exception of those from P2 (APAMLC) where moderate levels of contaminants were detected. Sediments from P7 and P9 (PEMLS) occasionally showed signs of petroleum hydrocarbons. The other sediments showed no relevant contamination but presented variable toxicity, es-

## Resumo

Este estudo analisou a qualidade dos sedimentos de três Áreas Marinhas Protegidas (AMP) situadas na porção central do litoral paulista (Parque Estadual Marinho da Laje de Santos - PEMLS; Parque Estadual Xixová-Japuí- PEXJ; Área de Proteção Ambiental Marinha do Litoral Centro - APAMLC). Quatro campanhas de coleta foram organizadas (Setembro/Outobro-2013; Janeiro-2014; Julho-2014; Janeiro-2015). Amostras de sedimento foram coletadas em 10 pontos ao longo das 3 AMP. As amostras foram analisadas para granulometria, carbono orgânico total, $CaCO_3$, metais, hidrocarbonetos alifáticos e policíclico aromáticos, e toxicidade de sedimento integral e interface sedimento-água. Análise de Componentes Principais foi utilizada na integração dos dados. A maioria das amostras exibiu baixa contaminação, exceto a amostra de P2 (APAMLC) onde níveis moderados de contaminantes foram detectados. Sedimentos de P7 e P9 (PEMLS) eventualmente apresentaram sinais de hidrocarbonetos de petróleo. As demais amostras não apresentaram contami-

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pecially those of bioclastic composition. The PCA indicated a contribution of the sediment properties to the toxicities, especially the $CaCO_3$. In bioclastic sediments, toxicity might be due to physical causes by or any indirect factor such as the presence of ammonia. It was concluded that both natural and anthropic factors are causing toxicity in sediments from the MPAs studied.

Descriptors: Toxicity, Metals, Hydrocarbons, Marine Protected Area, Sediment.

nação relevante, mas tiveram toxicidades variáveis, especialmente os sedimentos predominantemente bioclásticos. A PCA indicou forte contribuição das propriedades do sedimento, principalmente $CaCO_3$ e amônia, na geração da toxicidade, indicando que fatores naturais e/ou antrópicos podem estar induzindo a toxicidade nas AMP estudadas.

Descritores: Toxicidade, Metais, Hidrocarbonetos, Área Marinha Protegida, Sedimento.

## INTRODUCTION

Currently, due to the importance of coastal ecosystems, there is a global concern for the establishment of Marine Protected Areas (MPAs). According to KELLEHER et al. (1995), an MPA is defined as "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".

However, the simple establishment of an MPA may not be capable in itself of protecting these areas, because a set of actions and policies must be implemented in order to effectively provide protection for the marine ecosystems (JAMESON et al., 2002). Threats to the MPAs include both internal factors - such as fishing and overcrowding - and external ones - such as the presence of polluting sources in the vicinity of the MPA (KELLEHER et al., 1995). MPAs located near human activities have experienced the phenomenon of transboundary movements of chemicals (POZO et al., 2009; TERLIZZI et al., 2004) and a few recent studies have demonstrated the negative biological effects of contaminants due to pollution (DAVANSO et al., 2013; RODRIGUES et al., 2013, ARAÚJO et al., 2013; CRUZ et al., 2014; GUSSO-CHOUERI et al., 2015; NILIN et al., 2013). Therefore, knowing if and how contamination from external sources affects the environmental quality within MPAs emerges as a critical aspect that must be addressed for proper MPA management.

In Brazil, there is a national system of protected areas (NSPA) that defines different categories of Protected Areas (including the MPAs), based on the degree of protection desired (BRASIL, 2000). The NSPA also establishes guidelines and rules for managing protected areas (PAs) and enhancing their effectiveness; however, they are not fully complied with with regard to the majority of Brazilian coastal PAs and MPAs. Brazilian MPAs thus cover a range of situations that may be taken as examples of management problems or lack of effective protection.

In the State of São Paulo, a mosaic of marine and coastal PAs was established along the coast (SÃO PAULO, 2008a) for the purpose of putting conservation activities in proper order and seeking sustainable development along the coastal zone. The mosaic comprises three large Marine Protected Areas (MPAs), which overlap or surround other PAs of different categories. Some of these latter are situated on the central coast of the state, where different economic activities play the role of environmental stressors (ABESSA et al., 2008a). The region is also affected by the pollution generated in the metropolitan region of the Baixada Santista, which includes sewage, litter, effluents and industrial residues, and that generated by the activities of the Port of Santos. Large cargo ships that use the port normally ride at anchor along the coast, close to or actually within some of the region's MPAs. CLARK (2001) stated that toxic substances such as oil, biocides and other chemicals may be released or spilled from the ships, causing environmental contamination (THOMAS et al., 2002; THOMAS et al., 2000) and negative effects to non-target species (GODOI et al., 2003; YTREBERG et al., 2010). Moreover, the disposal of sediments dredged from the Port of Santos occurs near the MPAs, and it is not clear whether or not the currents may eventually carry the plumes of disposed sediments towards any of them.

Three MPAs are specifically of major concern, as they come under the influence of the anthropic activities: 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).

The PEMLS was created in 1993, with the aim of protecting the marine ecosystems of the southwestern Atlantic coast (São Paulo, 1993). It was the first marine park in the State and nowadays it is immersed inside the Itaguaçu sector of the APAMLC. The PEMLS is

considered a priority area for the conservation of rocky shore biodiversity (BRASIL, 2002). LUIZ-JUNIOR et al. (2008) have stated that the park is influenced by a regime that alternates warm waters, which favor larval development, and cold and nutrient rich waters derived from upwelling. These factors permit the development of a diverse and abundant marine life. The absence of other rocky reefs in the vicinity favors the large concentration of fish in the region. Sediments from PEMLS presented generally low concentrations of chemicals but in some samples, contaminants were reported to be higher than the background values or exceeding the regional sediment quality values (GOBBATO, 2012).

Of the MPAs situated on the central coast of São Paulo, only the XJSP has a management plan, which has not, however, been implemented. There is evidence that contaminants from various sources tend to be transported towards this area by coastal currents (ABESSA et al., 2008b; SÃO PAULO, 2010). Previous data for this MPA have shown toxicity in both surface and bottom water samples and sediments (SÃO PAULO, 2010), as well as sediment contamination (LAMPARELLI et al., 2001; MARTINS et al., 2008; ABESSA et al. 2008a; CAMARGO et al., 2015; ARAUJO et al., 2013) and oxidative stress in bivalves (Pereira et al., 2011; 2012).

The APAMLC consists of three sectors: Guaíbe, Itaguaçu and Carijó (São Paulo, 2008b). Few studies of this MPA have focused on environmental pollution and its effects (CESAR et al., 2014; TORRES et al., 2009; SOUSA et al., 2007) but they have shown poor quality close to the Moela Island and northeastward from it. Sediment contamination and toxicity have been identified and attributed to the disposal of dredged sediments and port activities.

Most of contaminants tend to adsorb to the particles and accumulate in the sediments (INGERSOLL, 1995); therefore this environmental compartment provides an accurate indication of the environmental pollution status. Because the MPAs are potentially influenced by contamination sources installed in the region, it is necessary to assess the environmental quality in order properly to identify pollution and its effects and thus provide sound information for decision making and especially for the future management plans of both PEMLS and APAMLC. Thus, this investigation sought to assess the sediment quality in three MPAs located on the central coast of São Paulo (XJSP, PEMLS and APAMLC), identifying possible risks to or effects on these MPAs' benthic species.

## MATERIAL AND METHODS

### Study Area

Sediments were collected at 10 sampling sites, including some within the XJSP, different sectors of the APAMLC and their vicinities, and the PEMLS (Figure 1, Table 1). The criteria for selecting these 10 sites took into consideration, at least theoretically, that some of them came under anthropic pressure and that others would be less influenced by them.

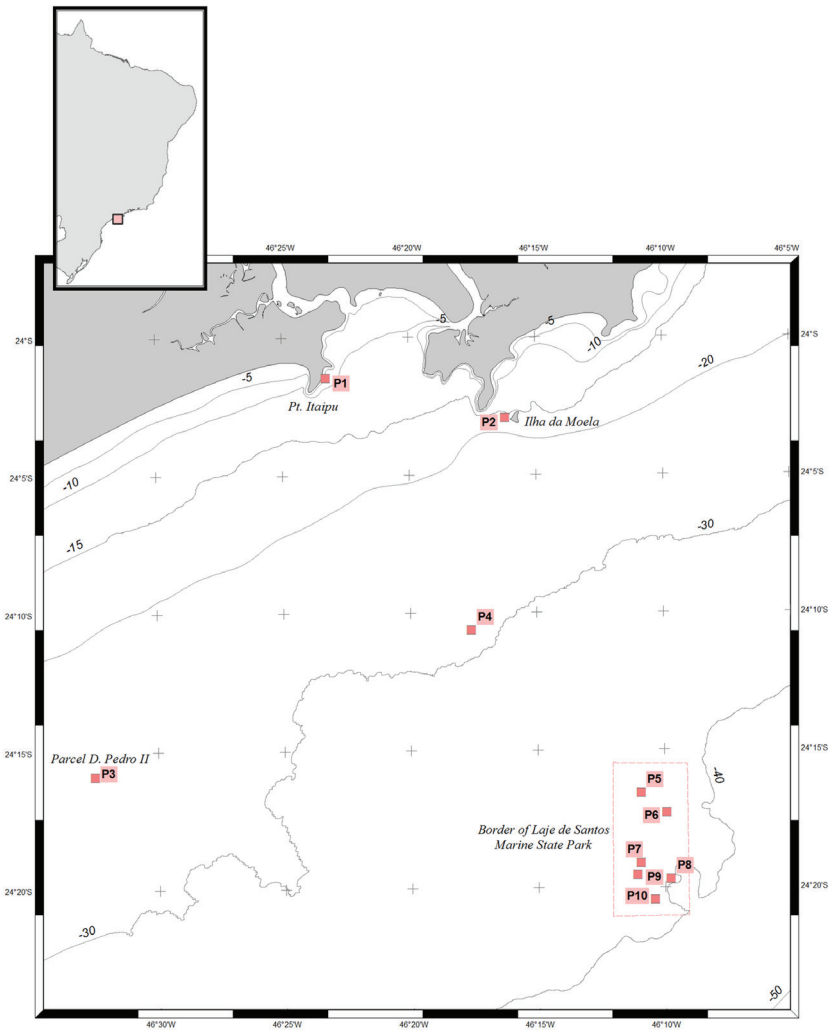



**Figure 1.** Map of the areas studied showing the sediment sampling sites.

**Table 1.** Characteristics of the sediment sampling sites of the three MPAs located on the central coast of São Paulo.

| Site | Location | Coordinates | Depth (m) | MPA | |
|---|---|---|---|---|---|
| | | E-UTM | N-UTM | | |
| P1 | Parcel dos Moleques | 358876 | 7342365 | 9 | XJSP |
| P2 | Ilha da Moela | 370868 | 7339746 | 20 | APAMLC |
| P3 | Parcel Dom Pedro | 343505 | 7315605 | 25 | APAMLC |
| P4 | Close to the disposal site of dredged material | 368674 | 7325527 | 20 | - |
| P5 | Parcel do Bandolim | 380013 | 7314669 | 35 | PEMLS |
| P6 | Parcel do Brilhante | 381749 | 7313355 | 15 | PEMLS |
| P7 | Laje de Santos | 380035 | 7309982 | 30 | PEMLS |
| P8 | Rochedos | 382040 | 7308928 | 35 | PEMLS |
| P9 | Parcel do Sul | 379806 | 7309168 | 20 | PEMLS |
| P10 | Parcel Novo | 380970 | 7307516 | 35 | PEMLS |

### Sediment collection

Four surveys were conducted for the sediment sampling, between 2013 and 2015. The first survey consisted of collections made on September 3rd, 2013 and 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 done on January 20th, 21st and 26th, 2015.

Sediments were collected by using a Van Veen grab sampler. The material retained in the sampler was thoroughly homogenized, and aliquots were separated for the analysis of grain size distribution, Total Organic Carbon (TOC), quantities of $CaCO_3$, metals, hydrocarbons and toxicity. Samples for the analyses of sediment properties and metals were transferred to plastic bags, while those for organic chemicals were transferred to metal recipients. Samples for the ecotoxicological analyses were stored in plastic flasks. On board, all the samples were kept preserved in ice. In the laboratory, samples for geochemical examination were preserved at -20 ºC, whereas those for toxicity tests were kept refrigerated at 4ºC. Additional samples of sediment were collected exclusively for ecotoxicological analysis (to be used as an internal control); these samples were collected for each survey on the Engenho D'Água Beach (Ilhabela, SP).

### Sediment characteristics

The physical properties of the sediments were analyzed by the SALT - Sea & Limno Technology Ltd (SALT Ambiental). Grain size distribution was measured by the wet-dry sieving method followed by pipetting to measure the different fractions of clays and silts (MUDROCH; MACKNIGHT, 1994), after freeze-drying and elimination of organic matter and $CaCO_3$ with hydrogen peroxide and hydrochloric acid 10%, respectively. Calcium carbonate contents ($CaCO_3$) estimation was conducted by HCl digestion and gravimetry (GRANT-GROSS, 1971). Decarbonated sediments were separated for total organic carbon analysis (TOC), and the analysis followed the method of oxidation with potassium dichromate described by GAUDETTE et al. (1974).

### Metals analyses

For major (Al and Fe) and trace (Hg, Cd, Co, Cr, Cu, Ni, Pb and Zn) metals analysis, sediments were digested with an acid solution containing 9 ml of HNO3 and 3 ml of HCl, according to the EPA 3051A protocol (USEPA, 1996) in a high pressure microwave system (CEM Corporation, model MDS—2000). Extracts were measured using the flame mode of a Fast- Sequential Atomic Absorption Spectroscope Varian, model Spectr-AAS-220-FS, with a deuterium lamp background correction for Pb, Ni and Hg. Levels of Hg were measured by cold vapor generation through coupling the spectrometer 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 analysis of two Standard Reference Materials (SRM 2704 - Buffalo River Sediment and SRM-1646a - Estuarine sediments), in three replicates. Details of these analyses can be seen in the Supplementary Material (available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing).

### Hydrocarbon analyses

The 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, according to UNEP (1991). 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 flame ionization detector (GC-FID). Thirty-three PAHs were quantitatively analyzed by an Agilent 6890 gas chromatograph coupled to a 5973N mass spectrometer (GC/MS) in a selected ion mode (SIM). The results of all the compounds analyzed are presented in the Supplementary Material (available at https://drive.google.com/drive/folders/17WQuKq2CjgyQzsM1xACJaGm50z12Dzja?usp=sharing).

Quality assurance and quality control (QA/QC) were based on the analysis of procedural blank, blank spike, matrix spike, matrix duplicate and standard reference material. The mean recoveries of surrogates and target compounds were within 65 and 102%. Precision ranged from 1.8 to 12% for AHs, and 1.6 and 19% for PAHs. The method's accuracy was ensured by the analyses of standard reference material from the International Atomic Energy Agency (IAEA 417). Method detection limit (MDL) was based on the standard deviation (3xσ) of seven replicates of a sediment sample containing target compounds at a level of one to five times the expected MDL.

### Toxicity Tests

Two approaches were used to assess the sediment toxicity: the chronic toxicity test exposing embryos of the sea urchin *Lytechinus variegatus* to the sediment-water interface (SWI) and the acute toxicity test with the burrowing amphipod *Tiburonella viscana*. For both, physical and chemical parameters (pH, salinity, dissolved oxygen and temperature) were checked at the beginning and end of each experiment. On the 4th campaign, the whole sediment toxicity test using the benthic copepod *Tisbe biminiensis* was also used to evaluate the sediment quality.

The Sediment-Water Interface test (SWI) was conducted following the method described by ANDERSON et al. (2001) and adapted by CESAR et al. (2004) for small volumes. This treatment assesses the effects of the contamination which rising from sediment may affect organisms in the adjacent water column. In this procedure the test system was set up in test tubes, containing sediment and water 1:4 (v:v). Then, the samples were tested for toxicity to sea urchin *L. variegatus* embryo-larval development according to the ABNT NBR 15350 protocol (ABNT, 2006). To achieve this, sea urchin spawning was induced and subsequent in vitro fertilization was done. The test was conducted by introducing approximately 400 embryos in each of four replicates, in addition to a negative control (filtered seawater). After the end of the test (24h), the embryos were analyzed microscopically for morphological abnormalities and delayed development.

The acute toxicity test with whole sediment (WS) with *Tiburonella viscana* was conducted in accordance with the protocol described by MELO and ABESSA (2002) and ABNT (2008). In this test, four replicates of each sediment sample were prepared in 1L-polyethylene test chambers that contained a 2-cm layer of sediment and 750ml of diluted seawater. After 24 hours, ten healthy adult and non ovigerous amphipods were introduced into each test chamber. The experiment lasted 10 days, and was kept under constant lighting and aeration, at a temperature of 25±2ºC. At the end of the test, the contents of each test chamber were sieved and the surviving organisms counted. Missing organisms were considered dead.

The sediment chronic toxicity tests used the copepod *Tisbe biminiensis* as test-organism, based on the protocol developed by ARAÚJO-CASTRO et al. (2009), with adaptations (photoperiod of 16:8 hours, whole sediment) proposed for tests with other harpacticoids (LOTUFO; ABESSA, 2002). Four replicates were set up for each sample and 10ml of high density polyethylene test-chambers filled with 2ml of sediment and 8ml of filtered sea water were used. Ten healthy ovigerous females were introduced into each replicate. The entire test system was incubated at 25±2ºC for 7 days. Next, the content of each replicate was fixed with formaldehyde (10%) and Rose-Bengal dye (0.1%). Finally, the number of adult females and their offspring (nauplii and copepodits) was counted using a stereomicroscope.

### Statistical Analysis

The results of the ecotoxicological assays were first checked for homocedasticity and normality by Bartlett's test and the Shapiro-Wilks test, respectively. Then, data from the acute sediment toxicity test were analyzed by the Student-t' test (for equal or unequal variances, depending on the case). Geochemical data were interpreted by observing exceedances to Canadian Sediment Quality Guidelines (SMITH et al., 1996) – considering Threshold Effect Levels (TEL) and Probable Effect Levels (PEL) - and also by comparison with local sediment quality values – SQVs (CHOUERI et al., 2009). Ecotoxicological and geochemical data were integrated by Principal Component Analyses (PCA); the multivariate techniques were run by using the PC-ORD software, after log-transformation and standardization of data prior to the analyses.

## RESULTS

### Sediment Properties

According to the sediment properties' analyses (Table 2), sediment samples from P1 and P4 were sandy, with low amounts of TOC and $CaCO_3$. Sediments from P2 were muddy (silty) and presented high quantities of TOC. Sediments collected at P3 and in the PEMLS (P5-P10) were sandy and presented $CaCO_3$ levels reaching 93%. A detailed description of sediment textures may be found in the Supplementary Material and in Moreira et al., (2017).

**Table 2.** Amounts of Total Organic Carbon (TOC), $CaCO_3$ and Mud (in %) in sediments collected from MPAs located on the Central Coast of São Paulo.

| Survey | | TOC (%) | | | | $CaCO_3$ (%) | | | | Mud (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | S1 | S2 | S3 | S4 | |
| Sampling sites | P1 | 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 | 0.36 | 3.68 | 2.59 | 1.96 | 7.7 | 8.71 | 12.11 | 13.49 | 100.01 | 100 | 97.12 | 91.2 | |
| | P3 | 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 | 0.22 | 0.19 | 0.07 | 0.12 | 3.28 | 3.1 | 4.06 | 3.68 | 0.3 | 0.26 | 0.38 | 2.49 | |
| | P5 | 0.29 | 0.14 | 0.21 | 0 | 26.97 | 8.94 | 5.45 | 5.44 | 0.72 | 0.41 | 0.74 | 3.56 | |
| | P6 | 0.31 | 0.22 | 0.21 | 0.21 | 6.55 | 2.5 | 2.6 | 78.8 | 0.62 | 0.57 | 1.2 | 24.93 | |
| | P7 | 0.49 | 0.49 | 0.2 | 0.28 | 58.07 | 77.64 | 78.5 | 80.07 | 2.51 | 4.16 | 2.79 | 11.03 | |
| | P8 | 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 | 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 | 0.31 | 0.19 | 0.11 | 0.24 | 7.07 | 2.56 | 4.85 | 27.06 | 0.74 | 0.86 | 1.44 | 7.25 | |

## Sediment Chemistry

Summarized lists of chemicals (metals, AHs and PAHs) and their respective concentrations in the sediments studied are shown in tables 3-6. In all the campaigns, sediments from P2 exhibited a moderate degree of contamination. Concentrations of Zn, Pb, Ni, Cr, Cu, Co and PAHs were often above local SQVs (CHOUERI et al., 2009). Sediments from P2 also presented concentrations of Zn, Pb, Ni, Cr, Fe, Al, Co and Cu above the regional backgrounds (LUIZ-SILVA et al., 2006; QUINÁGLIA, 2006). In the second survey, levels exceeding the TEL were observed for Ni, Cu, Hg and PAHs. All the sediments collected in the 1st, 2nd and 4th surveys presented levels of Pb above local SQVs, but this was an artifact due to the high analytical quantification limits for this element (<12 µg.g-1), which were higher than the SQV. Concentrations of Cd were below the detection limits in all the samples from all the surveys. In the other samples, the concentrations of metals were low.

The levels of AHs were higher in sediments from P2, and Unresolved Complex Mixture (UCM) was observed, indicating the presence of oil compounds that are resistant to degradation. On the other hand, the Carbon Preference Index (CPI) indicated a contribution of hydrocarbons from superior plants (see Moreira et al., 2017). Nevertheless, the sediments from P2 could be considered moderately contaminated by AHs and PAHs. Occasionally, sediments from station P9 presented abnormalities for ΣPAHs and ΣAHs, indicating a contribution of organic compounds to this region. Sediments from station P7 presented light HPAs, with 40.2% perylene.

## Sediment Toxicity

The physical-chemical parameters of the overlying waters within the test-chambers during the whole-sediment toxicity tests were considered appropriate, according to the criteria proposed by MELO and ABESSA (2002). The values ranged within the recommended intervals during the tests. The parameters are shown in the Supplementary Materials. On the 1st campaign, sediments from P3, P8 and P9 induced significantly higher mortalities among the amphipods, while on the 2nd campaign the samples from P4, P5 and P7 produced significant mortality rates. On the 3rd campaign, the amphipods exposed to the sediments from P2, P3, P5, P6, P8 and P9 exhibited significantly higher mortalities, but animals exposed to the samples P1, P7 and P10 had low survival rates (<50%). On the 4th campaign, only sediments P3 and P4 induced significantly high mortalities, but again, organisms exposed to sediments from P7 and P9 presented low survival rates (<50%). High variability between replicates was observed in all the tests, but was especially large in the experiments of the 3rd and 4th surveys and probably interfered with the statistical comparisons. These results are shown in Figure 2.

During the sediment-water interface toxicity tests with sea-urchin embryos (Figure 3), the water conditions were considered appropriate, and the physical chemical parameters of the overlying waters were in accordance with the criteria proposed by PRÓSPERI and ARAÚJO (2002). These data are shown in the Supplementary Materials. Unionized ammonia levels in the overlying waters of the test chambers were often above the toxic thresholds, especially for the bioclastic sediments, and probably interfered with the ISA toxicities. In the first campaign, sediments

from P2, P3, P5, P7, P9 and P10 caused a reduction of the embryonic development. The levels of unionized ammonia in the overlying waters were high for P2, P3, P5 and P10. On the 2nd campaign, sediments of P1, P2, P7 and P9 produced a decrease in the rate of embryonic development. Sediments P7 and P9 caused 100% abnormal development; in their replicates, despite the proper D.O. levels, the sediments presented the darkened aspect typical of hypoxia.

**Table 3.** Concentrations of metals, aliphatic hydrocarbons, n-alcanes and poly-aromatic hydrocarbons in sediments from MPAs located on the central coast of São Paulo, international Sediment Quality Guidelines, regional Sediment Quality Values and regional backgrounds, during the first survey (2013). All concentrations expressed in µg.g-1, with exception of Al and Fe which are expressed in %. Bold fonts indicate concentrations exceeding the TELs or SQVs.

| Sample | Zn | Pb | Ni | Cr | Fe | Al | Co | Cd | Hg | Cu | Σn-alcanes | ΣAliphatics | ΣHPA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P1 | 19.24 | <12 | <1.1 | 10.6 | 1.31 | 0.589 | 3.07 | <0.6 | <0.03 | <0.9 | 0.16 | 1.64 | 5.45 |
| P2 | 71.81 | 19.9 | 14.93 | 37.2 | 3.33 | 4.2 | 8.35 | <0.6 | 0.03 | 14.93 | 10.3 | 39.1 | 671 |
| P3 | 9.64 | <12 | <1.1 | 4.7 | 0.454 | 0.497 | <1.7 | <0.6 | <0.03 | 0.91 | 0.32 | 1.55 | 9.11 |
| P4 | 5.08 | <12 | <1.1 | 5 | 0.33 | 0.36 | <1.7 | <0.6 | <0.03 | <0.9 | 0.05 | 1.06 | <1 |
| P5 | 7.1 | <12 | <1.1 | 6.86 | 0.382 | 0.384 | <1.7 | <0.6 | <0.03 | <0.9 | 0.11 | 1.2 | <1 |
| P6 | 9.33 | <12 | 1.29 | 6.65 | 0.47 | 0.46 | 1.94 | <0.6 | <0.03 | <0.9 | 0.09 | 1.02 | <1 |
| P7 | 15.45 | <12 | 1.6 | 4.08 | 0.514 | 0.65 | <1.7 | <0.6 | <0.03 | 0.91 | 0.16 | 1.28 | 7.01 |
| P8 | 12.31 | <12 | 1.99 | 4 | 0.531 | 0.646 | <1.7 | <0.6 | <0.03 | 1.99 | 0.25 | 1.7 | 2.32 |
| P9 | 16.19 | <12 | 2.89 | 7.03 | 0.766 | 0.88 | 2.1 | <0.6 | <0.03 | 1.93 | 2.27 | 4.84 | 132 |
| P10 | 10.56 | <12 | <1.1 | 8 | 0.525 | 0.63 | 2.33 | <0.6 | <0.03 | <0.9 | 0.04 | 0.97 | <1 |
| TEL1 | 124 | 30.2 | 15.9 | 52.3 | - | - | - | 0.7 | 0.13 | 18.7 | - | - | 1684 |
| PEL1 | 271 | 122 | 42.8 | 160 | - | - | - | 4.21 | 0.696 | 108 | - | - | 16770 |
| SQV2 | 37.9<br>61.7 | 10.3<br>19.2 | 3.89<br>6.02 | 65.8 | - | - | 4.1<br>10.3 | 0.75 | 0.08<br>0.32 | 69 | - | - | 163<br>950 |
| BG3 | 51 | 15 | 14 | 31 | 2.9 | 2.1 | 7.3 | 0.11 | 0.12 | 14 | - | - | - |
| BG4 | 63.8 | <0.26 | 11.2 | 27.8 | - | - | 6.7 | <0.02 | <0.02 | 11 | - | - | - |

1 = SMITH et al. (1996); 2 = CHOUERI et al. (2009); 3 = LUIZ-SILVA et al. (2006); 4 = QUINÁGLIA (2006).

**Table 4.** Concentrations of metals, aliphatic hydrocarbons, n-alcanes and poly-aromatic hydrocarbons in sediments from MPAs located on the central coast of São Paulo, international Sediment Quality Guidelines, regional Sediment Quality Values and regional backgrounds, during the second survey (2014). All concentrations expressed in µg.g-1, with exception of Al and Fe which are expressed in %. Bold fonts indicate concentrations exceeding the TELs or SQVs.

| Sample | Zn | Pb | Ni | Cr | Fe | Al | Co | Cd | Hg | Cu | Σn-alcanes | ΣAliphatics | ΣHPA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P1 | 19.65 | <12 | 1.5 | 15.4 | 1.362 | 0.597 | 3.0 | <0.6 | <0.03 | <1.0 | 0.06 | 1.08 | 1.55 |
| P2 | 73.50 | 18.0 | 17.6 | 57.4 | 3.40 | 4.13 | 9.6 | <0.6 | 0.144 | 14.9 | 5.66 | 27.9 | 2023 |
| P3 | 3.70 | <12 | <1.5 | 5.0 | 0.24 | 0.188 | <3.0 | <0.6 | <0.03 | <1.0 | 0.04 | 0.71 | <1.00 |
| P4 | 4.78 | <12 | <1.5 | 5.8 | 0.312 | 0.218 | <3.0 | <0.6 | <0.03 | <1.0 | 0.05 | 1.02 | <1.00 |
| P5 | 6.01 | <12 | <1.5 | 8.4 | 0.328 | 0.259 | <3.9 | <0.6 | <0.03 | <1.0 | 0.06 | 0.55 | <1.00 |
| P6 | 8.09 | <12 | 1.8 | 11.8 | 0.478 | 0.39 | <3.0 | <0.6 | <0.03 | <1.0 | 0.06 | 0.65 | <1.00 |
| P7 | 19.00 | <12 | 2.5 | 7.8 | 0.486 | 0.498 | <3.0 | <0.6 | <0.03 | 1.6 | 0.15 | 0.56 | 3.58 |
| P8 | 8.70 | <12 | <1.5 | 11.2 | 0.474 | 0.381 | <3.0 | <0.6 | <0.03 | <1.0 | 0.15 | 0.68 | 1.47 |
| P9 | 5.43 | <12 | 2.00 | 7.4 | 0.231 | 0.164 | <3.0 | <0.6 | <0.03 | <1.0 | 0.42 | 1.26 | 19.9 |
| P10 | 9.00 | <12 | <1.5 | 12.6 | 0.492 | 0.44 | <3.0 | <0.6 | <0.03 | <0.9 | 0.16 | 1.35 | 17.0 |
| TEL1 | 124 | 30.2 | 15.9 | 52.3 | - | - | - | 0.7 | 0.13 | 18.7 | - | - | 1684 |
| PEL1 | 271 | 122 | 42.8 | 160 | - | - | - | 4.21 | 0.696 | 108 | - | - | 16770 |
| SQV2 | 37.9<br>61.7 | 10.3<br>19.2 | 3.89<br>6.02 | 65.8 | - | - | 4.1<br>10.3 | 0.75 | 0.08<br>0.32 | 69 | - | - | 163<br>950 |
| BG3 | 51 | 15 | 14 | 31 | 2.9 | 2.1 | 7.3 | 0.11 | 0.12 | 14 | - | - | - |
| BG4 | 63.8 | <0.26 | 11.2 | 27.8 | - | - | 6.7 | <0.02 | <0.02 | 11 | - | - | - |

1 = SMITH et al. (1996);. 2 = CHOUERI et al. (2009); 3 = LUIZ-SILVA et al. (2006); 4 = QUINÁGLIA (2006).

**Table 5.** Concentrations of metals, aliphatic hydrocarbons, n-alcanes and poly-aromatic hydrocarbons in sediments from MPAs located on the central coast of São Paulo, international Sediment Quality Guidelines, regional Sediment Quality Values and regional backgrounds, during the third survey (2014). All concentrations expressed in µg.g-1, with exception of Al and Fe which are expressed in %. Bold fonts indicate concentrations exceeding the TELs or SQVs.

| Sample | Zn | Pb | Ni | Cr | Fe | Al | Co | Cd | Hg | Cu | Σn-alcanes | ΣAliphatics | ΣHPA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P1 | 22.49 | <10 | 2.4 | 10 | 1.346 | 0.459 | 3.24 | <0.6 | <0.03 | 1.07 | 0.31 | 0.98 | 10.4 |
| P2 | 61.12 | 21.5 | 12.4 | 33.65 | 2.71 | 2.04 | 7.17 | <0.6 | <0.03 | 11.2 | 5.61 | 21.2 | 480 |
| P3 | 6.36 | <10 | <1.4 | 2.73 | 0.298 | 0.193 | <3 | <0.6 | <0.03 | <1 | 0.12 | 0.88 | 1.85 |
| P4 | 4.54 | <10 | <1.4 | 4.6 | 0.274 | 0.1662 | <3 | <0.6 | <0.03 | <1 | 0.01 | 0.68 | <1.00 |
| P5 | 6.32 | <10 | <1.4 | 6.2 | 0.302 | 0.198 | <3 | <0.6 | <0.03 | <1 | 0.01 | 0.72 | <1.00 |
| P6 | 8.81 | <10 | 1.4 | 7.19 | 0.409 | 0.253 | <3 | <0.6 | <0.03 | <1 | 0.01 | 0.69 | <1.00 |
| P7 | 13.39 | <10 | <1.4 | 2.77 | 0.206 | 0.184 | <3 | <0.6 | <0.03 | 1.2 | 0.07 | 0.99 | <1.00 |
| P8 | 12.23 | <10 | 2.3 | 7.4 | 0.584 | 0.401 | <3 | <0.6 | <0.03 | <1 | 0.19 | 1.04 | <1.00 |
| P9 | 10.31 | <10 | 1.4 | 5.6 | 0.514 | 0.29 | <3 | <0.6 | <0.03 | <1 | 0.44 | 1.55 | 8.12 |
| P10 | 9.04 | <10 | 1.4 | 6.61 | 0.437 | 0.261 | <3 | <0.6 | <0.03 | <1 | 0.02 | 0.73 | <1.00 |
| TEL1 | 124 | 30.2 | 15.9 | 52.3 | - | - | - | 0.7 | 0.13 | 18.7 | - | - | 1684 |
| PEL1 | 271 | 122 | 42.8 | 160 | - | - | - | 4.21 | 0.696 | 108 | - | - | 16770 |
| SQV2 | 37.9<br>61.7 | 10.3<br>19.2 | 3.89<br>6.02 | 65.8 | - | - | 4.1<br>10.3 | 0.75 | 0.08<br>0.32 | 69 | - | - | 163<br>950 |
| BG3 | 51 | 15 | 14 | 31 | 2.9 | 2.1 | 7.3 | 0.11 | 0.12 | 14 | - | - | - |
| BG4 | 63.8 | <0.26 | 11.2 | 27.8 | - | - | 6.7 | <0.02 | <0.02 | 11 | - | - | - |

1 = SMITH et al. (1996);. 2 = CHOUERI et al. (2009); 3 = LUIZ-SILVA et al. (2006); 4 = QUINÁGLIA (2006).

**Table 6.** Concentrations of metals, aliphatic hydrocarbons, n-alcanes and poly-aromatic hydrocarbons in sediments from MPAs located on the central coast of São Paulo, international Sediment Quality Guidelines, regional Sediment Quality Values and regional backgrounds, during the fourth survey (2015). All concentrations expressed in µg.g-1, with exception of Al and Fe which are expressed in %. Bold fonts indicate concentrations exceeding the TELs or SQVs.

| Sample | Zn | Pb | Ni | Cr | Fe | Al | Co | Cd | Hg | Cu | Σn-alcanes | ΣAliphatics | ΣHPA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P1 | 34.61 | <12 | 2.3 | 16.6 | 1.794 | 1.485 | 4.23 | <0.6 | 0.0295 | 4.27 | 1.360 | 2.58 | 85.8 |
| P2 | 74 | 16.1 | 14.4 | 35.33 | 3.02 | 4.05 | 9.07 | <0.6 | 0.103 | 15 | 5.040 | 22.7 | 624 |
| P3 | 7.92 | <12 | <1 | 1.42 | 0.285 | 0.345 | <3 | <0.6 | 0.0184 | 1.07 | 0.034 | 1.39 | <1.00 |
| P4 | 7.92 | <12 | <1 | 5.6 | 0.345 | 0.363 | <3 | <0.6 | 0.0086 | <1 | 0.005 | 0.78 | <1.00 |
| P5 | 9.49 | <12 | <1 | 4.5 | 0.349 | 0.35 | <3 | <0.6 | 0.0152 | 1.05 | 0.049 | 1.36 | 4.54 |
| P6 | 15.84 | <12 | <1 | 5 | 0.586 | 0.655 | <3 | <0.6 | 0.015 | <1 | 0.210 | 1.68 | 26 |
| P7 | 17.23 | <12 | <1 | 3 | 0.363 | 0.462 | <3 | <0.6 | 0.0104 | <1 | 0.160 | 2.00 | 13.1 |
| P8 | 9.51 | <12 | <1 | 5.6 | 0.48 | 0.498 | <3 | <0.6 | 0.0146 | <1 | 0.074 | 1.21 | 4.51 |
| P9 | 13.34 | <12 | <1 | 2.8 | 0.642 | 0.667 | <3 | <0.6 | 0.0302 | <1 | 0.170 | 1.53 | 19.1 |
| P10 | 12.6 | <12 | <1 | 7.2 | 0.619 | 0.577 | <3 | <0.6 | 0.0154 | <1 | 0.049 | 1.01 | 6.14 |
| TEL1 | 124 | 30.2 | 15.9 | 52.3 | - | - | - | 0.7 | 0.13 | 18.7 | - | - | 1684 |
| PEL1 | 271 | 122 | 42.8 | 160 | - | - | - | 4.21 | 0.696 | 108 | - | - | 16770 |
| SQV2 | 37.9<br>61.7 | 10.3<br>19.2 | 3.89<br>6.02 | 65.8 | - | - | 4.1<br>10.3 | 0.75 | 0.08<br>0.32 | 69 | - | | 163<br>950 |
| BG3 | 51 | 15 | 14 | 31 | 2.9 | 2.1 | 7.3 | 0.11 | 0.12 | 14 | - | - | - |
| BG4 | 63.8 | <0.26 | 11.2 | 27.8 | - | - | 6.7 | <0.02 | <0.02 | 11 | - | - | - |

1 = SMITH et al. (1996);. 2 = CHOUERI et al. (2009); 3 = LUIZ-SILVA et al. (2006); 4 = QUINÁGLIA (2006).

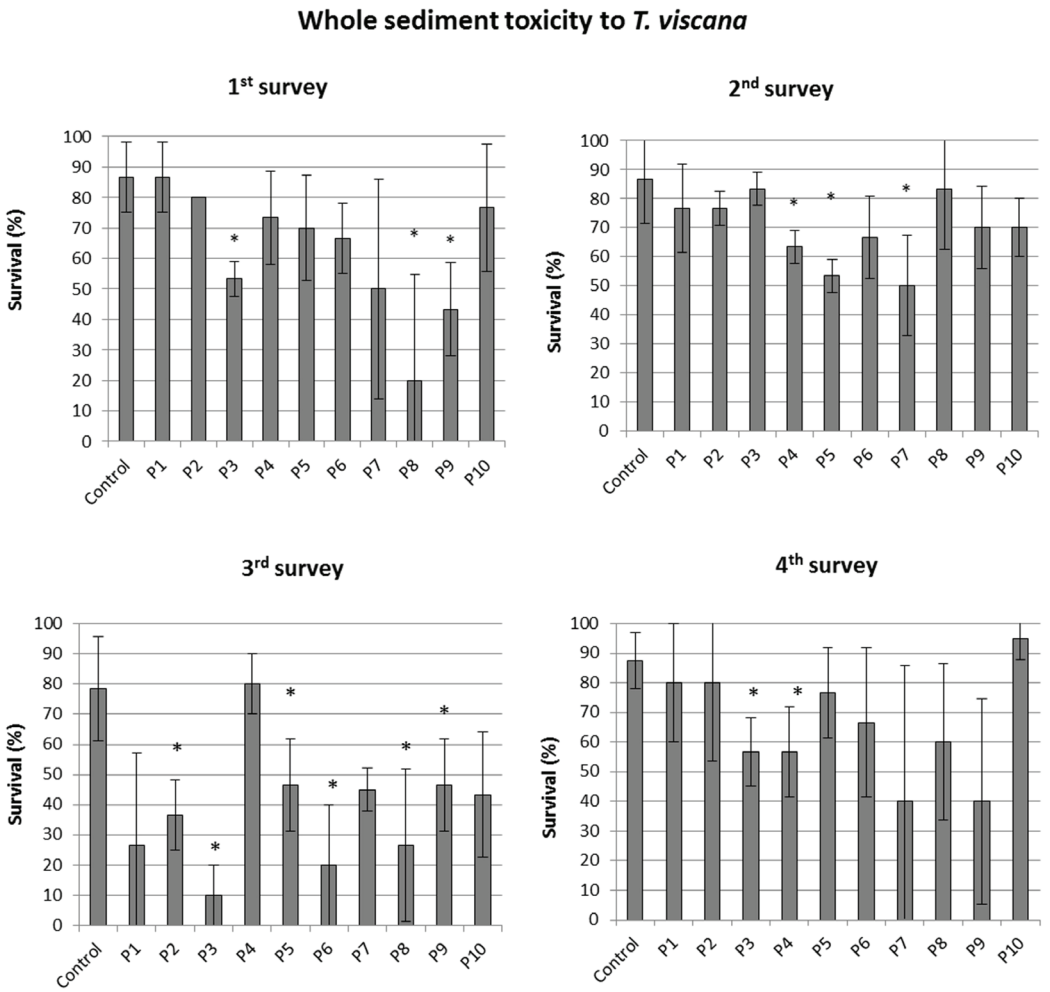



**Figure 2.** Survival of *Tiburonella viscana* exposed to sediments from three Marine Protected Areas located on the central coast of São Paulo (Brazil). * indicates significant differences for the controls ($p<0.05$).

On the third campaign significant adverse effects were observed in the organisms exposed to the sediments from P2, P3, P5, P6, P7, P8, P9 and P10. Embryos exposed to sediments from P1 exhibited a low rate of development (<30%). Potentially toxic levels of unionized ammonia were observed in the overlying waters of the test-chambers for P2, P3, P6, P7, P8 and P9, thus ammonia may have contributed to the observed effects. Great variability between replicates in this test suggests that interfering factors may have affected the results. On the 4th campaign, the embryonic development rates in P2, P3, P6 and P9 were significantly lower than the controls. The development rates of the embryos exposed to sediments from P4, P5, P7 and P10 were low, but due to the high variances, they were not considered significantly lower than those of the controls.

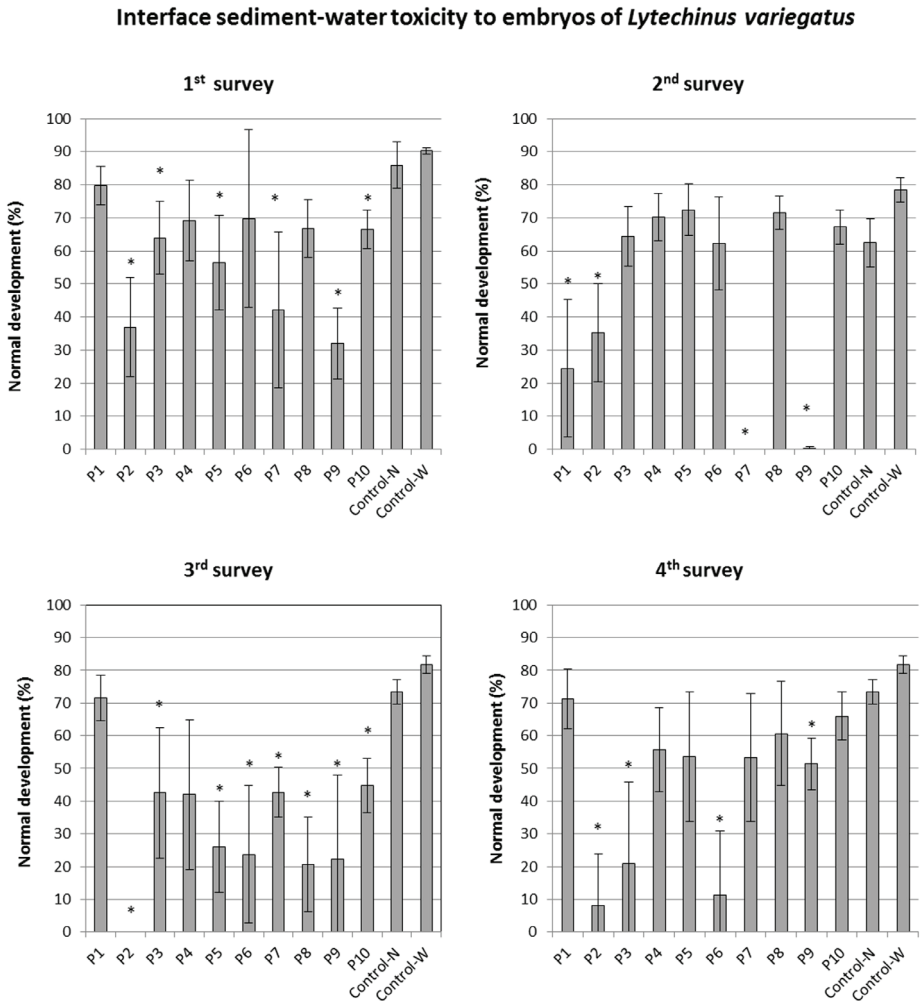



**Figure 3.** Normal embryonic development of *Lytechinus variegatus* exposed to sediments from three Marine Protected Areas located on the central coast of São Paulo (Brazil) by sediment-water interface (SWI). * indicates statistical differences in comparison to the controls ($p<0.05$).

In the chronic toxicity test with whole-sediments and copepods, the conditions of the overlying waters in the test-chambers were considered appropriate and in accordance with the ranges proposed by ARAÚJO-CASTRO et al. (2009). For more details, see the Supplementary Material. No sediment sample was considered toxic to *T. biminiensis* (Figure 4).

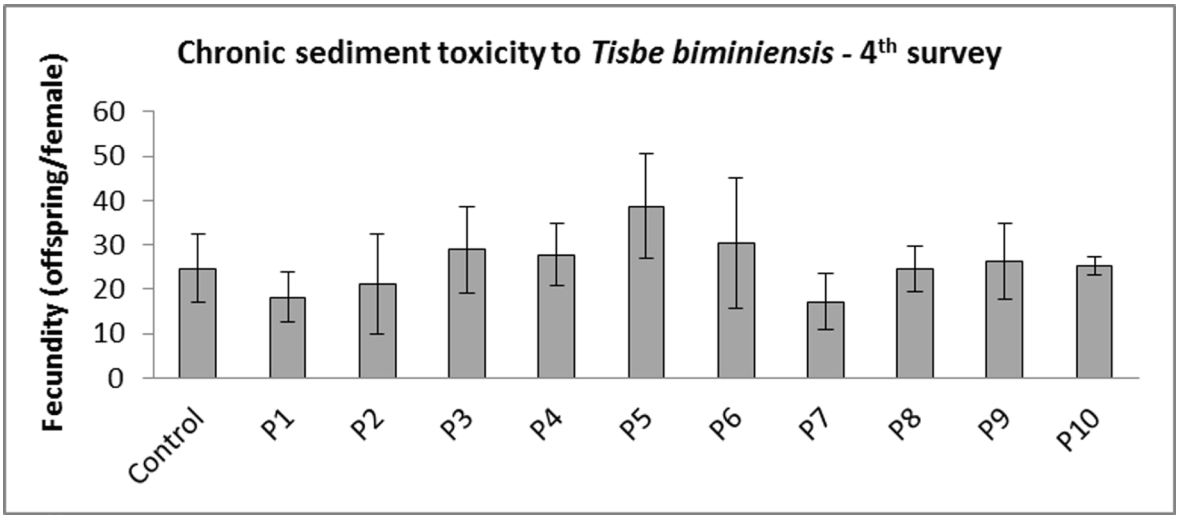



**Figure 4.** Fecundity of *Tisbe biminiensis* exposed to sediments from three Marine Protected Areas located on the central coast of São Paulo (Brazil).

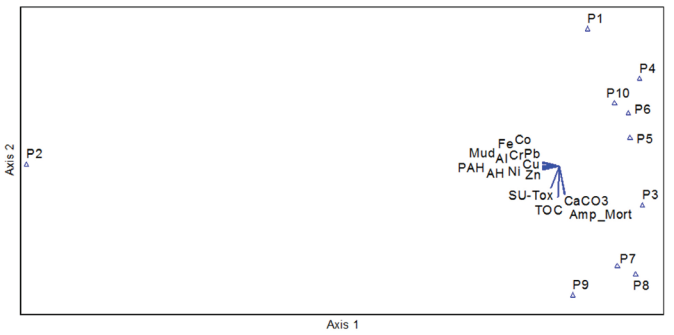
## Data Integration

The PCAs with geochemistry and ecotoxicological data showed relatively similar results for each survey (Figure 5). Details of these analyses are shown in the Supplementary Material. Variances were accounted for by the first two axes (Principal Components – PCs). Generally, the first axes associated metals, HAs, PAHs, TOC and muds (excepting the 1st PCA, where TOC correlated only to the second axis). Chronic toxicity to sea-urchin embryos presented lower correlation to the first axis, in the 2nd, 3rd and 4th surveys. On the other hand, the second axes showed association of acute toxicity to amphipods and $CaCO_3$ in all the surveys. Chronic toxicity to sea-urchin embryos correlated to the 2nd axis in the first and second surveys.

In all the PCAs, P2 was strongly associated with axis 1 and positioned alone. The other sites tended to separate due to the $CaCO_3$ contents. An exception occurred for P7 and P9 on the second survey (due to high toxicity and the presence of PAHs and detectable levels of Cu and Ni); such signs of contamination in these sediments occurred only on the 2nd survey.

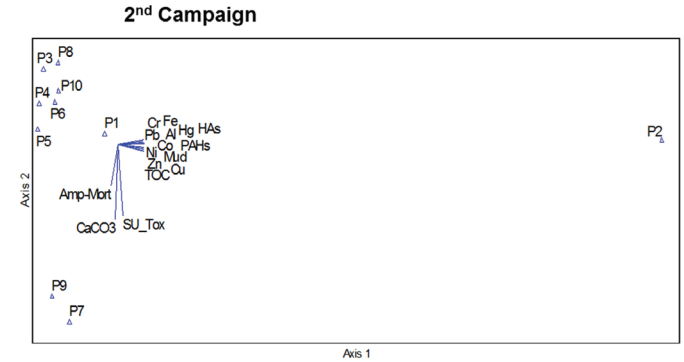
**1st Campaign**

| Samples | PC1 | PC2 |
|---|---|---|
| Eigenvalues | 11.23 | 2.90 |
| Var (%) | 74.87 | 19.33 |
| Cum. Var (%) | 74.87 | 94.20 |
| Zn | -0.99 | -0.04 |
| Pb | -0.99 | 0.01 |
| Ni | -0.99 | -0.10 |
| Cr | -0.99 | 0.14 |
| Fe | -0.97 | 0.08 |
| Al | -0.99 | -0.07 |
| Co | -0.99 | 0.12 |
| Cu | -0.99 | -0.06 |
| Mud | -0.99 | -0.05 |
| COT | -0.07 | -0.95 |
| $CaCO_3$ | 0.28 | -0.85 |
| HA | -0.99 | 0.04 |
| PAH | -0.99 | -0.09 |
| Amphipod Mortality | 0.32 | -0.87 |
| Sea-Urchin Toxicity | -0.51 | -0.67 |



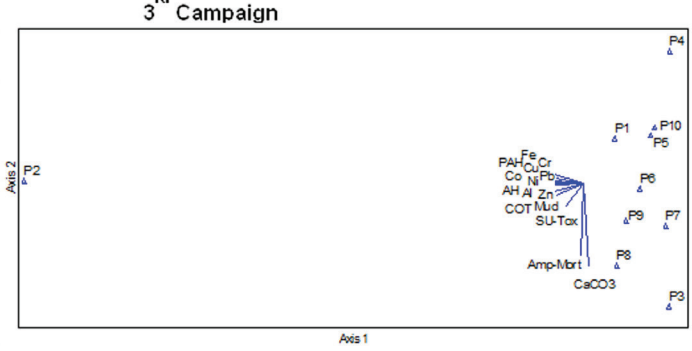

**2nd Campaign**

| | PC1 | PC2 |
|---|---|---|
| Eigenvalues | 12.85 | 2.02 |
| Var (%) | 80.32 | 12.64 |
| Cum. Var (%) | 80.32 | 92.96 |
| Zn | 0.98 | -0.09 |
| Pb | 0.99 | 0.02 |
| Ni | 0.99 | -0.04 |
| Cr | 0.99 | 0.06 |
| Fe | 0.97 | 0.04 |
| Al | 1.00 | 0.01 |
| Co | 0.97 | 0.03 |
| Cu | 0.99 | -0.06 |
| Hg | 0.99 | 0.02 |
| Mud | 0.99 | -0.04 |
| $CaCO_3$ | -0.12 | -0.95 |
| TOC | 0.99 | -0.07 |
| AH | -0.99 | 0.02 |
| PAH | -0.99 | 0.01 |
| Amphipod Mortality | -0.26 | -0.52 |
| Sea-Urchin Toxicity | 0.19 | -0.90 |




**3rd Campaign**

| | PC1 | PC2 |
|---|---|---|
| Eigenvalue | 12.07 | 1.34 |
| %var | 80.47 | 8.96 |
| Cum Var % | 80.47 | 89.43 |
| Zn | -0.97 | -0.01 |
| Pb | -0.99 | 0.01 |
| Ni | -0.99 | 0,00 |
| Cr | -0.99 | 0.09 |
| Fe | -0.94 | 0.06 |
| Al | -0.99 | -0.01 |
| Co | -0.99 | 0.03 |
| Cu | -0.99 | 0.01 |
| AH | -0.99 | 0,00 |
| PAH | -0.99 | 0.02 |
| Mud | -0.97 | -0.11 |
| TOC | -0.99 | -0.08 |
| CaCO3 | 0.21 | -0.84 |
| Amphipd Mortality | -0.06 | -0.74 |
| Sea-Urchin Toxicity | -0.61 | -0.23 |




**4th Campaign**

| | PC1 | PC2 |
|---|---|---|
| Eingenvalue | 13.16 | 1.68 |
| Var % | 77.41 | 9.89 |
| Cum Var % | 77.41 | 87.3 |
| Zn | 0.98 | -0.04 |
| Pb | 0.98 | -0.04 |
| Ni | 0.99 | -0.01 |
| Cr | 0.97 | 0.15 |
| Fe | 0.95 | 0.07 |
| Al | 0.99 | -0.01 |
| Co | 1,00 | 0.03 |
| Hg | 0.98 | -0.06 |
| Cu | 1.00 | 0.04 |
| AH | 0.98 | -0.06 |
| PAH | 0.99 | -0.03 |
| Mud | 0.94 | -0.28 |
| TOC | 0.99 | -0.07 |
| CaCO3 | -0.18 | -0.9 |
| Amphipd Mortality | -0.51 | -0.74 |
| Sea-Urchin Toxicity | 0.51 | -0.28 |
| Copepod Toxicity | 0.32 | -0.33 |

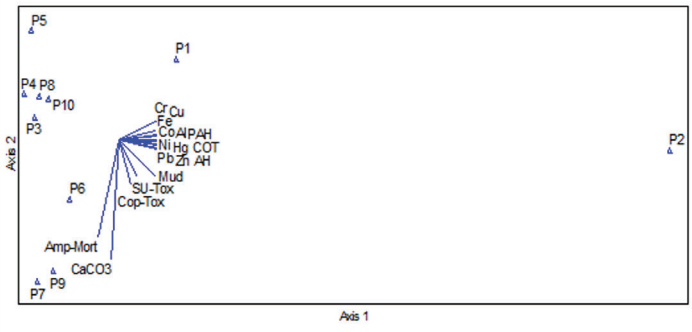



**Figure 5.** Results of the Principal Component Analyses using geochemistry and ecotoxicological data, for all the sampling surveys. Eigenvalues and correlations to the PC are also shown.

## DISCUSSION

To better discuss the data, firstly we decided to consider each area separately: A) PEMLS (P5, P6, P7, P8, P9, P10); B) Moela Island, in the Guaibe sector of the APAMLC (P2); C) the Carijó sector of the APAMLC (P3); D) the vicinity of the disposal site of dredged sediments (P4), and E) XJSP (P1).

The results obtained within the PEMLS were within the ranges previously observed in the region by GOBATTO (2012). In general, concentrations were low and only in P9 and P7 occasionally higher values were found for AHs and PAHs. The concentrations of metals were compared to those obtained for the Alcatrazes Archipelago (São Sebastão) and Palmas and Cabras islands (Ubatuba), part of a restrictive protected area described by HOFF et al. (2015). The sediments from the PEMLS presented concentrations ranging from the level of those observed in Alcatrazes (background for outer islands of São Paulo) or higher, and were often more similar to those observed at the Palmas and Cabras Islands. However, GOBATTO (2012), from a more detailed exploration of his results, identified some geochemical abnormalities related to some elements, which would indicate inputs from external sources (such as ships anchored in the vicinity, the disposal of dredged sediments, and/or land-based activities) or even internal sources (recreational or fishing boats). That same author also discussed the possibility that some elements could be accumulating in the south of the park, corroborating our results for P9, where AHs and PAHs were occasionally observed. According to FONTES et al., 2017, the model of oceanic circulation shows the region of P9 and P7 shadowed, thus we may infer that these sites may accumulate fine particles and contaminants under certain conditions.

Further in the PEMLS, HASHIMOTO (2012) analyzed the toxicity of the same samples as GOBATTO (2012) and observed sediment toxicity, attributed to natural factors: the texture and bioclastic nature of the sediments could explain the effects on *T. viscana*, whereas the high levels of ammonia explain the effects on *L. variegatus* embryos. The presence of contaminants, as occasionally shown in P7 and P9, appeared to be of minor importance.

For the P2 (Moela Island), previous data indicated environmental degradation in the region (ABESSA et al., 2008; TORRES et al., 2009; CESAR et al., 2015). Besides, a previous study conducted by FUNDESPA (2008) had identified sediment contamination and toxicity close to Moela Island. Therefore, our results confirm the poor quality of the sediments in this area.

For P3, however, there are no previous data on the sediment quality. Sediments from this site presented similar characteristics to those observed on other islands of São Paulo, such as high percentages of biogenic $CaCO_3$, low quantities of muds and TOC, and low concentrations of metals and organic compounds. Toxicity was observed, probably caused by natural factors, as $CaCO_3$ (for *T. viscana*), and unionized ammonia (for *L. variegatus*). ANKLEY et al. (1990) have discussed the role of ammonia as an important toxicant in toxicity tests.

The sediments collected in the area located between the disposal site of dredged materials and the PEMLS (P4) presented low concentrations of metals and hydrocarbons. This result is similar to that observed by FUNDESPA (2008) and GOBATTO (2012). However, FUNDESPA (2008) detected sediment toxicity and alteration of the benthic communities. CESAR et al. (2014) reported sediment contamination by PCBs close to P4; these authors also observed sediment toxicity, which was associated with nutrients, metals As, PAHs, PCBs, phthalates and Aldrin. Sediment toxicity close to P4 was also observed by HASHIMOTO (2012). TORRES et al. (2009) observed low concentrations of contaminants but registered occasional toxicity in sediments. In fact, as the dredged materials include sediments from regions with greatly varying levels of contamination and grain size, and the disposal of these sediments is done in a dispersive region where currents are variable, a broad variation of sediment quality is to be expected at P4. This region requires further study to identify the causes of toxicity and to model the possibility of sediment transport from the disposal site under different oceanographic and climatic conditions.

In the sediments from XJSP (P1), the levels of contaminants tended to be higher than those observed in the PEMLS, but they were below the legal standards and the regional backgrounds. Previous data for this area showed toxicity and sediment contamination for Cu, Cd and Zn (SÃO PAULO, 2010; ARAÚJO et al., 2013), and negative effects on Perna perna bivalves (PEREIRA et al., 2011; 2012). The literature also reports sediment contamination by hydrocarbons, Hg, Pb, Zn, Cu (LAMPARELLI et al., 2001), detergents and sterols (MARTINS et al., 2008) and toxicity of water and sediments (ABESSA et al. 2008a; 2008b). Sewage and urban drainage have been reported as the main pollution sources in XJSP (AMBROZEVICIUS; ABESSA, 2008; LAMPARELLI et al., 2001). Moreover,

CAMARGO et al. (2015) assessed the toxicity of the sediments of XJSP using advanced techniques and stated that the main causes of toxicity were the combination of ammonia and metals. Those authors also commented that sewage was the main source of contaminants in that area and that other emerging contaminants such as pharmaceuticals and personal care products were to be expected. The large variation in toxicity may be caused by climatic and oceanographic factors such as the low pressure fronts that bring storms and extra-tropical storms that produce groundswells; the waves thus originated are capable of resuspending and transporting superficial sediments, as had previously been observed in a neighboring area (ABESSA et al., 2005). However, under normal conditions, contaminants tend to be transported towards the west portion of Santos Bay by coastal currents (SÃO PAULO, 2010) and accumulate in the region of XJSP.

The detection of sediment contamination and toxicity in the MPAs studied corroborates the findings of previous studies conducted in other areas (NILIN et al., 2013; GUSSO-CHOUERI et al., 2015) and confirms that MPAs can be partially or totally affected by pollution. TERLIZZI et al. (2004) investigated PCB levels in 15 MPAs in Italy, only a few of them, however, presented worrying levels of PCBs. We would also stress that the MPAs located closer to the more impacting anthropic activities tended to exhibit worse conditions as is only to be expected: HALPERN (2014) stated that MPAs tend to be effective in protecting marine life when age, size, isolation, protection and enforcement are present. Our results also highlight the necessity of studying pollution in MPAs worldwide.

In the case of the MPAs of the central coast of São Paulo, this study shows that a combination of natural factors and anthropic contaminants is causing sediment toxicity, especially in XJSP and APAMLC. In the PEMLS, further studies are required to identify the causes of the toxicity found.

## ACKNOWLEDGEMENTS

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