

## Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments from the Itajaí-Açu estuarine system

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### Introduction

Polycyclic aromatic hydrocarbons (PAH) are a large group of organic compounds with two or more fused aromatic rings. PAH may enter the marine environment through several routes including atmospheric deposition, river runoff, domestic and industrial outfalls and direct spillage of petroleum or petroleum products. Inputs from natural sources are usually low when compared to those from anthropogenic sources<sup>1</sup>. In aquatic environments, PAH are readily adsorbed onto particulate matter, and sediments act as a reservoir for these hydrophobic contaminants.

The Itajaí-Açu estuarine system, located in southern Brazil, is affected by industrial and dredging activities. In this study PAH in surface sediment samples were evaluated to identify their sources.

### Results and discussion

A total of twelve surface sediment samples (0-10 cm depth) were collected at the Itajaí-Açu estuarine system in July 2011. All experimental conditions were based on reports of previous studies<sup>2</sup>. The following PAH compounds were found in the sediment samples: naphthalene, methyl naphthalenes, acenaphthylene, acenaphthene, fluorene, methylfluorenes, phenanthrene, methylphenanthrenes, anthracene, fluoranthene, pyrene, methylpyrenes, benzo [b] fluoranthene and benzo [a] pyrene.

Total concentration of PAH, expressed as the sum of the compounds listed above, ranged from 63.89 to 1458.99 ng g<sup>-1</sup> dry weight (Table 1). Highest concentrations were observed at sites 1, 2, 5 and 6, located around the Itajaí harbor and Itajaí shipyard with total PAH concentration higher than 500 ng g<sup>-1</sup>. Concentrations > 500 ng g<sup>-1</sup> are indicative of relatively highly contaminated samples, while samples with 250 ng g<sup>-1</sup> < total PAHs < 500 ng g<sup>-1</sup> are classified as fairly contaminated<sup>3</sup>. In this sense, four sediment samples (Sites 1, 2, 5 and 6) are classified as highly contaminated and one sediment sample (Site 4) is classified as fairly contaminated. Alkyls PAH were also identified at all sampling sites. The highest alkyl contributions were detected at sites 9 and 11, suggesting a strong influence of fossil fuels to the sediments. Sources of PAH were

evaluated. Phenanthrene is more thermodynamically stable than anthracene, so the ratio Phe/Ant is observed to be very high in PAH petrogenic pollution, but lower in pyrolytic contamination cases.

**Tabela 1.** Total concentrations of PAH, total alkyl PAH and ratios between PAH (Phen: phenanthrene; Ant: anthracene; naph: naphthalene)

| Station | ΣPAH<br>ng g <sup>-1</sup> dry<br>weight | Σ Total<br>Alkyl PAH<br>(%) | Σ Methylnaph/<br>naph<br>ng g <sup>-1</sup> dry<br>weight | Phen/Ant |
|---------|--|-----------------------------|---|----------|
| 1       | 970.95                                   | 7.5                         | -   | 1.24     |
| 2       | 692.32                                   | 19.8                        | -   | 6.75     |
| 3       | 235.72                                   | 36.5                        | -   | 0.83     |
| 4       | 281.03                                   | 26.4                        | 0.89  | 2.26     |
| 5       | 527.96                                   | 16.3                        | 1.62  | 0.76     |
| 6       | 1458.99                                  | 15.0                        | 0.76  | 3.29     |
| 7       | 63.89                                    | 33.5                        | 1.21  | -        |
| 8       | 84.44                                    | 20.4                        | 0.78  | 1.37     |
| 9       | 125.82                                   | 71.0                        | 4.19  | -        |
| 10      | 112.30                                   | 38.8                        | -   | 1.06     |
| 11      | 156.57                                   | 81.8                        | -   | -        |
| 12      | 92.04                                    | 51.4                        | 1.88  | -        |

The ratio Phe/Ant could be calculated for some stations due to the absence of one or both compounds. For those sites calculated, values were < 10 indicating pyrolytic input. The dominance of alkylated homologs of naphthalene at stations 5, 7, 9 and 12 was indicative of fresh petroleum sources. Thus, considering the ratios and the presence of alkyl PAH, PAH in Itajaí-Açu estuarine system were originated from mixed sources such as petroleum and its combustion products.

### Conclusions

PAH in the sediment samples from the Itajaí-Açu estuarine system are originated from petrogenic and pyrolytic sources. Fossil fuels from the ships and fisher boats and their combustion are potential sources.

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