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Revisiting hydrocarbons source appraisal in sediments exposed to multiple inputs

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ABSTRACT

The aim of this work was to test the efficiency of statistical methods as compared to the traditional diagnostic ratios to improve hydrocarbon source identification in sediments subjected to multiple inputs. Hydrocarbon determination in Guanabara Bay sediments pointed out high degradation and ubiquitous petrogenic pollution through the presence of high unresolved complex mixture. Polycyclic aromatic hydrocarbon (PAHs) ratios suggested pervasive contamination derived from combustion in all sediments and failed discriminating samples despite the specificity of sources in different sampling sites. Principal component analysis (PCA) effectively distinguished the petrogenic imprint superimposed to the ubiquitous combustion contamination, since this technique reduces the influence of PAHs distribution which is common to all samples. PCA associated to multivariate linear regression (MLR) allowed a quantitative assessment of sources confirming predominance of the pervasive contaminant component superimposed to a generalized petrogenic imprint. The pervasive component derives from combustion contributions as well as from differential PAHs degradation.

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Although Guanabara Bay has been one of the most studied Brazilian coastal ecosystems over the last years (Christensen et al., 2010; Wagener et al., 2012, 2010; Luz, 2007; Soares-Gomes et al., 2010; Meniconi et al., 2002; Meniconi, 2007; Brito et al., 2006; Azevedo et al., 2004; Carreira et al., 2002), the lack of continuous observations and the complexity of such system associated to a megalopolis prevents understanding key factors required for suitable management. The densely populated hydrographic basin of about 4500 km[2] houses a large industrialized area. The lack of appropriate conservation policy is responsible for the bay chronicle pollution condition. The alterations in the drainage basin initiated by the beginning of the 19th century led to highly eutrophic condition, high sedimentation rates, elevated concentration of toxic metals and hydrocarbons in sediments, and changes in the pelagic and benthic communities (Hamacher, 1996; Lima, 1996; Ribeiro, 1996; Amador, 1997; Feema, 1998; Valentin et al., 1999). Since the intensification of offshore oil exploration in the 1990s the bay has been increasingly used as a basis for activities of the oil industry. This triggered a growing concern on the possible environment impacts derived from such activities.

The contribution of oil is characterized by the presence of *n*-alkanes covering a wide range of molecular weight non-preferred carbon numbers. Besides petrogenic origin, aliphatic hydrocarbons can be synthesized by marine and terrestrial organisms. The main biogenic sources are represented by terrestrial plants, phytoplankton and bacteria.

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The continental inputs of natural aliphatic hydrocarbons consist mainly of cuticular waxes of vascular plants, characterized by long carbon chains and odd carbon numbers, predominantly composed of n-C27, n-C29 or n-C31 (Eglinton et al., 1962; Eglinton and Hamilton, 1967). The contribution by terrestrial higher plants is evidenced by the distribution of odd n-alkanes in the range n-C23 to n-C35. The *n*-alkanes odd-numbered carbon chains also are synthesized primarily by marine biota, but in this case are shorter chains (n-C15 and n-C21) (Bouloubassi and Saliot, 1993). Once in the environment, weathering causes loss of light compounds (particularly those smaller than n-C14), through evaporation of intermediate compounds and loss of heavy ones, mainly by degradation.

Polycyclic aromatic hydrocarbons (PAHs) which are present in petroleum and combustion residues comprise a large group of organic compounds formed by two or more fused aromatic rings. These compounds, with carcinogenic and mutagenicity properties, are widely found in sediments around the world with concentrations increasing in areas under influence of urban centers (Laflamme and Hites, 1978). As consequence of human activity, PAHs concentration in sediment cores show progressively increases in time (Silliman et al., 2001) which parallels the growth in anthropogenic input since the 19th century (Pereira et al., 1999; Borges et al., 2009).

Hydrocarbons produced from different source have unique characteristics determined by several factors. The first studies targeting hydrocarbon source appraisal have shown that specific source properties could be used as a tool to determine the origin of these compounds in the environment (Cooper and Bray, 1963; Clark and Blumer, 1967; Blumer et al., 1971; Simoneit, 1985; Youngblood and Blumer, 1975; Wakeham et al., 1980a–c; Boehm and Farrington, 1984; Benner et al., 1990; Benner and Gordon, 1989; Prahl and Carpenter, 1983; Gschwend and Hites, 1981; Sicre et al., 1987; Baumard et al., 1998). Hydrocarbons are found in petroleum or derivatives but are also produced in the incomplete combustion of organic matter and are naturally generated in the environment. This diversity of sources allied to the complexity of environmental systems hampers the unambiguous identification of a certain source in marine sediments, especially when near to urban areas. Therefore, many qualitative studies have reported the incidence of hydrocarbons from so-called "combined sources" in different marine sediments (Laflamme and Hites, 1978; Youngblood and Blumer, 1975; Wakeham et al., 1980a,b) and are of little use for setting strategies for source abatement.

Understanding the provenance of hydrocarbons, in especial of the polycyclic aromatic hydrocarbons (PAHs) in complex systems such as Guanabara Bay, requires development and testing of multiple tools and approaches. One of the most commonly used approaches relies on diagnostic ratios and is sustained on the assumption that each source is associated with relative proportions of species that are unique, and the species in question are conserved from the source to the point of measurement. Since this assumption is not enough robust, one single ratio cannot be used for source identification but rather a combination of ratios. Even in this case source appraisal is not always successful (Wagener et al., 2011, 2012) and gives no information on the relative importance of different sources.

Multivariate methods have been used to support source assignment due to data complexity (Li et al., 2012; Wagener et al., 2012; Christensen et al., 2010; Chen et al., 2012; Barakat et al., 2011). The most frequently used statistical methods are the hierarchical cluster and the principal component analysis (PCA). Hierarchical cluster analysis is a multivariate statistical procedure that starts with a data set containing information about a sample of entities and attempts to reorganize these entities into relatively homogeneous groups (Aldenderfer and Blashifield, 1984). Principal component analysis, on the other side, is a statistical method where a large number of independent variables can be systematically reduced to a smaller, conceptually more coherent set of variables by linear combination (Dunteman, 1989). Besides these statistical procedures other factorial and regression analysis are used in the attempt to distinguish sources, such as principal component analysis associated with multiple linear regression (PCA-MLR) and factor analysis with non-negative constraints (FA-NNC) (Sofowote et al., 2008; Chen et al., 2012; Li et al., 2012, 2009; Wang et al., 2009).

The aim of the present work was to revisit the issue of source appraisal in a marine system subjected to multiple sources of hydrocarbon and test the performance of different approaches.

Surface sediments (2 cm) were sampled in April 2012 using a van Veen sampler. Eleven different sites were selected in the Guanabara Bay as to cover a wide area (Fig. 1) taking into consideration previous studies and activities carried out in the bay. Some sampling sites for which data were obtained after an oil spill in January 2000 (Meniconi et al., 2002) and in a two years monitoring program from 2005 to 2007 (Wagener et al., 2012) were revisited.

Station 6, located in northwest region receives inputs from rivers heavily polluted by sewage, litter and industrial residues. This region also houses the second largest refinery in Brazil, where an oil spill occurred in 2000 after a pipeline rupture. Station 2 is located near to Rio de Janeiro harbor and there the highest historical concentrations of PAH in Guanabara Bay are registered (Meniconi, 2007; Wagener et al., 2012). Station 7 is in an environmental protection area while the other stations are located widespread in the bay.

EPA 8015C and EPA 8270C were the adopted methods for the quantification of aliphatic and aromatic compounds, respectively. All samples were processed in duplicate using two different sediment masses, 5 g and 2 g, to check the method linearity. Samples were Soxhlet extracted (EPA 3540C) in dichloromethane over 24 h after addition of the surrogate standards n-dC30 and p-terphenyl-d14.

The hydrocarbons fractions were separated in a glass column (1.3 cm i.d. and 30 cm height) packed with cooper, anhydrous Na_2SO_4, alumina and silica. The aliphatic (F1) and aromatic (F2) fractions were eluted with n-hexane and dichloromethane:hexane (1:1), respectively. Both extracts were concentrated to 1 mL under N_2 stream and internal standards (F1 – n-C24d and F2 – mixture containing naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12) were added to the fractions.

PAHs were determined by gas chromatography coupled to mass spectrometry (GC–MS) while n-alkanes in the range of n-C12 to n-C40, the isoprenoids pristane and phytane, the unresolved complex mixture (UCM) and the resolved peaks (RP) were determined by gas chromatography with flame ionization detector (GC-FID). The PAHs determined were the 16 priority PAHs of United States Environmental Agency (USEPA), dibenzothiophene, perylene and alkylated homologs of naphthalene, fluorene, phenanthrene, chrysene, pyrene and dibenzothiophene. Quantifications were based on internal standard addition and calibration curves.

Average recoveries were $90 \pm 13\%$ for p-terphenyl-d14 and $113 \pm 21\%$ for n-dC30. Detection limits were 0.4 ng g^{-1} for PAH and 10 ng g^{-1} for n-alkanes. The difference between total concentrations of duplicate samples was below 15% therefore the concentrations reported in the present study refer to the largest sample mass (5 g) considered more representative. However, when compound concentration was above the upper limit of the calibration curve for PAHs analysis, the reported values refer to the 2 g aliquot. Accuracy was verified by the successful analysis of the SRM 1944, a reference material.

Results for the aliphatic and aromatic fractions are shown in Tables 1 and 2. Table 3 shows the summarized information on