THE STATUS OF WATER AND SEDIMENT SAMPLES FROM GUANABARA BAY – RIO DE JANEIRO: A PRELIMINAR STUDY CONSIDERING PCDD/F CONTAMINATION

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Introduction

The Guanabara Bay, Rio de Janeiro, has over 50 miles of shoreline and at least 12 major surface water inlets that introduce industrial and/or domestic waste. As part of a larger study to characterise the environmental condition of the waters and sediments within the Bay it is thought that a comprehensive evaluation of the condition of waters and sediments in the Cunha Channel and its many inputs would provide several benefits [1]. The Cunha channel is situated at the UFRJ campus and represents a considerable source of pollution in the city of Rio de Janeiro. To date, little work have been performed to characterise and remediate the contamination of the channel. One effort has been the plantation of "mangue" trees to absorb part of the metals present in the water . Some boat industries, as well as a hospital and two research centers are located at the margins of the channel. These buildings, together with other polluted rivers opening into the channel and the university itself may be, in part, responsible for the contamination of Cunha channel.

Water and sediment samples from the Cunha channel have been analysed for the presence of POPs according to modified US EPA methodologies. Thus, sample extracts were examined by gas chromatography-mass spectrometry (GC-MS and GC-HRMS) techniques for the presence of individual phenols, chlorinated hydrocarbons, polynuclear aromatic hydrocarbons, organochlorine pesticides, PCBs and PCDD/Fs.

From the above it has been demonstrated that the input of organic matter to the waters and sediments of the Cunha channel derives from multiple sources, including natural bacterial, algae and higher plant matter, fossil fuels, domestic and industrial waste and untreated sewage.

This paper describes the identification and quantitation of some of the organic compounds present in water and sediment samples, incluidind polychlorinated dibenzodioxins and furans. Furthermore, the samples were examined for the presence of components diagnostic of both autogenic and anthropogenic input to the waters and sediments.

Methods and Materials

Water and sediment samples were collected from the Cunha channel at differnte locations and extracted with methylene chloride and concentrated to 1 mL in a Kuderna Danish system. For semivolatile compounds, USEPA 8270B protocols were followed. The final extract was then analysed by GC/MS, using firstly full-scan mode followed by Selected Ion Monitoring for the

determination of some selected pesticides at low levels (sub ppb). Components that were detected were quantitated using deuterium labelled internal standards and where possible using calibration curves generated from the response of authentic standard compounds against these internal standards. For PCB determination, the extracts were eluted through a silica-sulphuric acid column, and the resulting extracts analysed by High Resolution mass Spectrometry. The PCDD/F content was determined in sediment samples, acccording to USEPA 8290 methods. Isotope dilution techniques were applied, and the samples were extracted in Soxhlet during 16 hours, followed by silica-acid column and finally florisil treatment. The final extract was also injeteced in a DB-5 MS column coupled to a Micromass Ultima which operated at 10,000 resolution.

Results and Discussion

Figure 1 shows typical Total Ion Current (TIC) chromatograms of water and sediment total extracts following GC/MS analysis.

Fig 1a

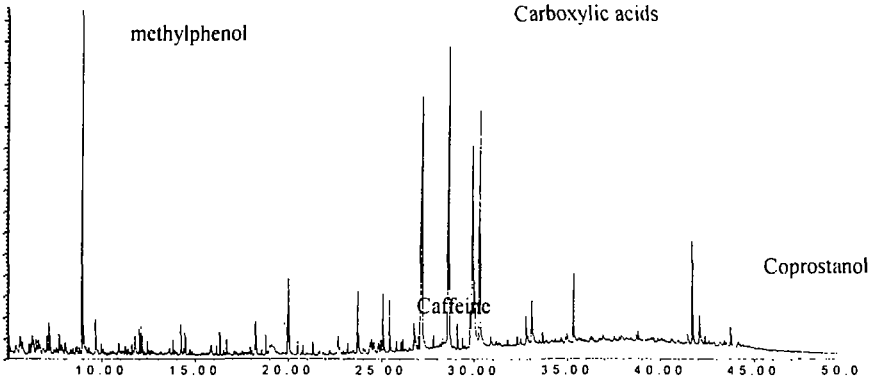

Fig 1b

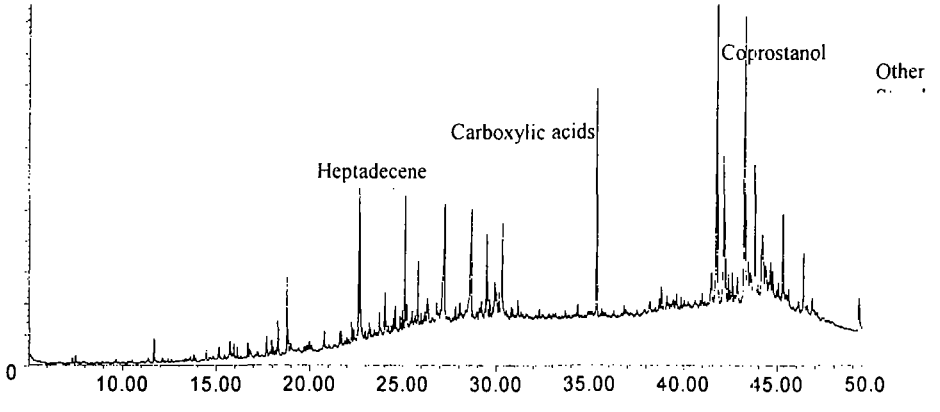

Figure 1 - Typical Chromatograms of water (a) and sediment (b) samples

The water samples contained a series of phenols ranging in concentration from ca. 1ppb to greater than 400 ppb. The dominant phenol component present was 4-methyl phenol (440 ppb) and is almost certainly present as a result of industrial pollution. Major amounts of carboxylic acids were detected in these samples ranging in carbon number from ca. C_{12} to C_{18} and maximising at C_{16} and consisted of saturate, mono and diunsaturated species. The distribution of these species is consistent with a bacterial origin [2].

The presence of major amounts of elemental sulphur, and organosulphur species again suggests a significant influence of sulphate reducing bacteria in the water. Other components present included caffeine suggesting either industrial or domestic waste input to the organics in the water. Major amounts of sterols were detected in the waters, dominated by the presence of coprostanol (5β(H) dihydrocholesterol). Coprostanol has been used as an indicator of the presence of sewage waste in sediments and waters. Thus, the presence of this and other sterols in the waters of the Cunha channel suggests a major input of untreated sewage waste. The only organochlorine pesticides detected were α ad β hexachlorocyclohexanes (HCH) the dominant isomer being the β HCH (Lindane) at concentration levels of ca. 0.2 ppb. PCDD/F were detected in sediment samples ranging from 0.9 to 2.2 ng/g I-TEQ. The congener distribution is presented in figure 2. PAH were detected ranging from naphthalene (10ppb) to chrysene (0.2ppb). No higher PAH were detected. Table 1 shows some of the compounds detected in both water and sediment samples including the polynuclear aromatic hydrocarbons known as the EPA 16 PAH, as an example of specific compound targetting.

Table 1 - Concentrations of selected components in water and sediment samples

Compound	Amount in Water (ppb)	Amount in Sediment
Naphthalene	9.87	6.58 µg/kg
Acenaphthylene	0.11	0.017 µg/kg
Acenaphthene	0.12	1.01 µg/kg
Fluorene	0.16	1.78 µg/kg
Phenanthrene	0.19	8.74 µg/kg
Anthracene	0.01	1.21 µg/kg
Fluoranthene	0.05	13.03 µg/kg
Pyrene	0.06	17.97 µg/kg
Benzanthracene	0.03	6.72 µg/kg
Chrysene	0.02	6.44 µg/kg
Benz(b)fluoranthene	n.d	9.16 µg/kg
Benz(k)fluoranthene	n.d	3.83 µg/kg
Benz(a)pyrene	n.d	10.42 µg/kg
Dibenz(ah)anthracene	n.d	5.58 µg/kg
Inden(1,2,3cd)pyrene	n.d	0.98 µg/kg
Benzo(ghi)perylene	n.d	7.94 µg/kg
Phenol	20.11	n.d.
4-Methylphenol	439.49	n.d.
Lindane	0.18	0.5 µg/kg
Caffeine	5.9	n.d.
Coprostanol	18.2	190 µg/kg
Total PCDD/F	Not analysed	2.2 ng/g I-TEQ

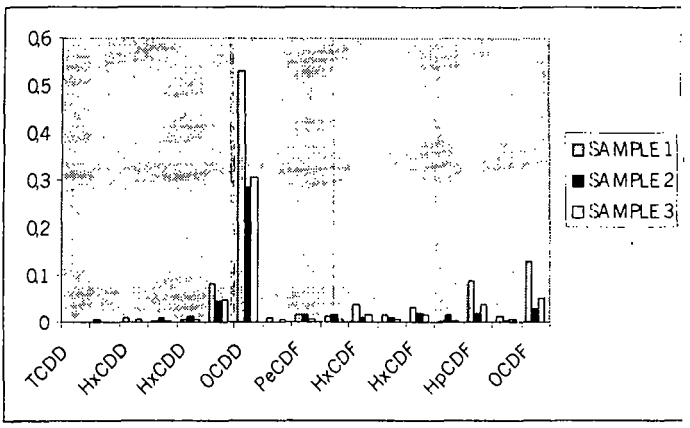

Figure 2 – PCDD/F congener distribution in sediment samples

The sediment samples again contained major amounts of carboxylic acids and sterols (including coprostanol) demonstrating the presence of both bacterial and sewage waste input. Other components present were saturated hydrocarbons, the distributions of which clearly demontrated fossil fuel origin and unsaturated hydrocarbons, such as heptadecene, known to be a dominant component of some species of algae. Phytadienes (diunsaturated isoprenoids) , known degradation products of phytol, the alcohol side chain of chlorophyll (green pigment of plants), were also present in relatively high concentrations suggesting again either an algal origin or a higher plant origin.

References

1. Carvalhaes, G.K. & Brooks, P.W. ; The distribution of hydrocarbons and other components in waters and sediments from the Guanabara Bay, Rio de Janeiro, *American Association of Petroleum Geologists. International Conference and Exhibition, Rio de Janeiro, RJ. Extended abstracts p. 652-653* (1998)

2. Carvalhaes, G.K. & Brooks, P.W. ; Resultados preliminares da análise de amostras de água e sedimento do Canal do Cunha (Rio de Janeiro) *Congresso Brasileiro de Geoquimica, 6., Salvador, BA, v. 1, p. 305-308* (1997)