Continental Shelf Research 71 (2013) 37–44

Contents lists available at ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

Research papers

Aliphatic and polycyclic aromatic hydrocarbons and trace elements as indicators of contamination status near oil and gas platforms in the Sergipe–Alagoas Basin (Southwest Atlantic Ocean)

Rafael A. Lourenço [a,*], Marcus A.G. Araujo Júnior [b], Ruy O. Meireles Júnior [b], Leandro F. Macena [b], Eleine Francioni de A. Lima [b], Maria Eulalia R. Carneiro [b]

[a] *Pontifícia Universidade Católica (PUC-Rio), Rua Marques de São Vicente, 225, 22451-900 Rio de Janeiro, RJ, Brazil*
[b] *Centro de Pesquisa e Desenvolvimento Leopoldo Miguez de Mello (Petrobras), Av. Horacio de Macedo, 950, 21941-915 Rio de Janeiro, RJ, Brazil*

ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form
13 September 2013
Accepted 16 September 2013
Available online 7 October 2013

Keywords:
Pollution
Oil platforms
Anthropogenic effects
Brazilian Coast
PAH

ABSTRACT

Oil and gas platforms from Sergipe–Alagoas Basin located in the northeastern region of Brazil do not discharge produced water. However, those platforms can be a potential source of contaminants to the marine environment due to their producing activities. In this study, sediment samples were collected in the vicinity of two offshore oil and gas platforms located in Sergipe–Alagoas Basin (PCM-9 and PGA-1) to evaluate the source and levels of hydrocarbons and trace elements (As, Fe, Al, Ti, Cu, Cd, Zn, Pb, Ni, Mn, Ba, V, Cr and Hg). Also, the potential impact of those platforms on the sediment quality was investigated. Polycyclic aromatic hydrocarbons diagnostic ratios observed in the sediment samples indicated hydrocarbons from pyrogenic source, specifically from biomass combustion. Trace elements As, Cd and Ba recorded concentrations higher than Threshold Effect Levels (TEL) in the sediment nearby the platforms. Also, there was evidence of some samples enriched by barium. Although As, Cd and Ba concentrations were higher than TEL, they most likely corresponded to background levels. The obtained results indicated that activities of the PCM-9 and PGA-1 platforms may not be affecting the quality of nearby sediment.

1. Introduction

The oil and gas (O&G) exploration on the Brazilian continental shelf was initiated in 1968, in the Guaricema field, located in the Sergipe–Alagoas Basin. Nowadays there are six fields producing oil and gas in the Sergipe–Alagoas Basin (Fields Camorim, Caioba, Dourado, Guaricema, Paru and Salgo), which all together account for a Volume of Oil In Place (VOIP: the total volume of oil in the reservoirs) of 168.1 million cubic meters and an oil production of 479 m^3 day^{-1} (ANP, 2011), that corresponds to 0.2% of Brazilian oil production. Actually, the fields have become quite depleted, reflecting a sharp decline in the production.

The main environmental threats associated with the oil and gas industry are the produced water (PW), a byproduct of oil and gas exploration and production, the drilling fluids and the drilling cuttings transported to the surface during oil well drilling. However, once the construction of the platform is completed, the input of drilling fluids and drilling cuttings to the environment ceases. Also, some of the offshore platforms send their produced water to treatment in the continent which is subsequently disposed of in the sea through outfalls, minimizing the impact of produced water discharges on the marine environment. This is the case of oil and gas platforms from Sergipe–Alagoas Basin. Thus, all PW are previously treated and discharged through outfall PAP-1. However, although platforms from Sergipe–Alagoas Basin do not discharge produced water they are potential sources of contaminants in the marine environment due to their activities.

Hydrocarbons can be originated from petroleum inputs, partial combustion of fossil fuels, forest fires and from the diagenetic degradation of biogenic precursors. Due to their high chemical stability and hydrophobicity, hydrocarbons tend to get adsorbed into particulate material and be deposited in the sediments (Readman et al., 2002). The evaluation of hydrocarbons in the environment is mainly based on analysis of aliphatic hydrocarbons (AH), especially n-alkanes and polycyclic aromatic hydrocarbons (PAH). Aliphatic hydrocarbons associated with petrogenic sources present a complete sequence of short and long chain n-alkanes, while aliphatic hydrocarbons from vascular plants are characterized by long molecular chains with an odd number of carbons (n-C_{23} to n-C_{35}; predominantly n-C_{27}, n-C_{29} and n-C_{31}) (Eglinton and Hamilton, 1967). Polycyclic aromatic compounds are intimately

---

* Corresponding author. Current address: CENPES/PDEDS/AMA – Centro de Pesquisa e Desenvolvimento Leopoldo Américo Migues de Mello (PETROBRAS), Av. Horacio de Macedo, 950, 21941-915 Rio de Janeiro, RJ, Brazil. Tel.: +55 2186880887.
E-mail address: rafaell@usp.br (R.A. Lourenço).

0278-4343/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.csr.2013.09.015

associated with anthropogenic sources, such as accidental oil spills, discharges from industrial effluents, and partial combustion and pyrolysis processes (Colombo et al., 1989). These compounds can be divided into two main groups: (a) low-molecular-weight PAH ($MW < 202$) with 2–3 aromatic rings that are associated with petrogenic sources and (b) high-molecular-weight PAH ($MW \geq 202$) that are frequently associated with the combustion process (Yunker et al., 2002).

Trace elements such as As, Ba, Cd, Cr, Cu, Ni, Pb, Hg and Zn occur naturally in the Earth's crust; however, because most of these elements are used in industrial activities, they are often found in elevated concentrations near industrial sites. Trace elements can also be found in the produced water. PW generated from early production has significantly higher trace metal content than that from mature fields (OGP, 2005). Thus, natural and anthropogenic contributions to trace element concentrations must be differentiated (Santos et al., 2005).

The recent oil and gas fields discovered in the southwestern Atlantic Ocean, in the vicinity of Brazilian coast, led to great concerns about the potential environmental impact related to offshore oil and gas platforms. However there was a lack of information, once few chemical data were published, particularly regarding organic and inorganic contaminants in the sediment around oil and gas platforms from Brazilian Coast. The aim of this study was to evaluate the contamination status in the sediment around two oil and gas platforms located at Sergipe–Alagoas Basin in the northeastern region of Brazilian Coast. The target contaminants were trace elements, aliphatic and polycyclic aromatic hydrocarbons. The results of this study may guide future researches about environmental contamination related to O&G production activities.

2. Study area

This study was conducted near two offshore oil and gas platforms (PCM-9 at 15 m deep and PGA-1 at 27 m deep) located in the Sergipe–Alagoas Basin in northeastern Brazil (Fig. 1). The water generated in the Sergipe–Alagoas Basin oil fields is sent to the mainland for treatment and is subsequently disposed of into the sea through an outfall. Thus, none of the generated water is released into the sea near the platforms. Both platforms have been active for more than 24 years.

The land–sea interface at the Sergipe coast includes the drainage basin of the São Francisco River, the biggest river in northeast Brazil, and numerous small river basins (e.g., the Vaza-Barris River basin, the Sergipe River basin) whose influence is partially masked by the São Francisco River. In addition, anthropogenic impacts such as from urbanization, aquaculture, agribusiness and the construction of dams on the São Francisco River, have significantly changed the coastal conditions (e.g., resulting in a dramatic decline of many marine fisheries) (Knoppers et al., 1999). Thus, watersheds of the Sergipe–Alagoas Basin, where the oil and gas platforms operated by Petrobras Brazil's state-led oil company are located, are susceptible to being impacted by anthropogenic activities.

3. Sampling and analytical methods

3.1. Sediment sampling

To evaluate organic compounds and trace metal inputs from natural and anthropogenic sources near the oil platforms, sediment samples were collected in triplicate from 12 sites around the PCM-9 platform and 12 sites around the PGA-1 platform. Reference areas were chosen for the two platforms using the following criteria: (a) areas that were 3 km away from the PGA-1 site and 8 km away from PCM-9 site, (b) areas that were far from drilling wells and (c) areas that had particle size characteristics similar to the sediment found near the platforms. The sites for each reference area were chosen randomly within a 500 m radius (Fig. 1 and Table 1). Sediments were sampled with a stainless steel box core. The top 2 cm of undisturbed surface sediment was placed into a clean aluminum can and into plastic bags for organic marker and trace element analyses, respectively. Samples were stored at –20 °C.

3.2. Grain size

Sediment samples were oven-dried for 36 h at 80 °C. Chloridric acid and hydrogen peroxide were used to remove organic matter and carbonates. Grain size distribution was determined on an ATM Model L3P Sonic Sifter Separator.

3.3. Organic markers

Aliphatic hydrocarbons (n-C_{10} to n-C_{40}) and PAH were analyzed following the procedures described in Method 3540 of the SW-846 series (USEPA, 1996). Approximately 10 g of wet sediment mixed with 20 g of sodium sulfate was Soxhlet extracted over 4 h using 200 mL of dichloromethane (DCM). A mixture of surrogates was added prior to sample extraction; n-$C_{12}d_{26}$, n-$C_{20}d_{42}$, n-$C_{24}d_{50}$ and n-$C_{30}d_{62}$ were used to represent AH, and p-terphenyl-d_{14} and 2-fluorobiphenyl were used to represent PAH. The DCM extract was purified using the column chromatography with 5% deactivated alumina (10 g) and silica (20 g). Elution was performed with 50 mL of n-hexane (fraction 1 – AH) and 200 mL of a (1:1) DCM/n-hexane mixture (fraction 2 – PAH). n-$C_{16}d_{34}$ was used as an internal standard for AH quantification. Naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} were used as internal standards for PAH quantification.

The analytical procedure described in Method 8015 of the SW-846 series (USEPA, 1996) was used to assess the concentrations of AH. The analyses were performed with an Agilent GC (model 6890) equipped with a flame ionization detector and an Agilent 19091J-412 (HP5) capillary fused silica column coated with 5% phenyl–methylpolysiloxane ($length = 30$ m, $ID = 0.32$ mm, film $thickness = 0.25$ μm). Injector and detector temperature was adjusted to 300 °C. Helium was used as the carrier gas. The following oven temperature program was used for AH: 60 °C for 1.5 min, 60–315 °C at a ramp rate of 6 °C min^{-1} and 315 °C for 10 min. The splitless mode was adopted. The compounds were individually identified by matching the retention time to the results obtained from standard mixtures of (C10–C40) n-alkanes. Concentrations of individual compounds were obtained using the internal standard peaks area method and a 5-point calibration curve for individual components (1.0–50.0 μg mL^{-1}, $r > 0.995$). Unresolved complex mixture (UCM) was calculated using the mean response factors of n-alkanes.

The instrumental analysis procedure described in Method 8270D of the SW-846 series (USEPA, 2007) was used to evaluate the concentration of PAH. The analyses were performed with an Agilent GC (model 7890A) coupled to a mass spectrometer detector (model 5975C) and an Agilent 122–5532 column (DB-5MS) ($length = 30$ m, $ID = 0.025$ mm, film $thickness = 0.25$ μm). Helium was used as the carrier gas. Injector temperature was adjusted to 300 °C. The following oven temperature program was used for PAH: 40 °C for 2.0 min, 40–100 °C at a ramp rate of 25 °C min^{-1}, 100–230 °C at a ramp rate of 5 °C min^{-1}, 230–270 °C at a ramp rate of 2 °C $min^{-}1$, 270 °C for 5.0 min and 270–320 °C at a ramp rate of 5 °C min^{-1}. The splitless mode was adopted. Mass