

Aliphatic and polycyclic aromatic hydrocarbons in surficial sediments of Bahía de Todos Santos, B. C., México.

A. Villegas Jiménez¹,
J. V. Macías Zamora²
y J. A. Villaescusa Celaya¹

¹Universidad Autónoma de Baja California. Instituto de Investigaciones Oceanológicas. Apdo. 453 Ensenada, Baja California, México.

²To whom correspondence should be sent

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ABSTRACT

The levels of concentration and distribution patterns of aliphatic (n-hydrocarbons) and polycyclic aromatic hydrocarbons (or PAH's) were determined in 16 samples of recent marine sediments of Bahía de Todos Santos, Baja California. The purpose was to establish base line data as a future reference. We report here on our findings. The extraction was carried out by means of a solid phase extraction procedure reported by Burrows (1983) both for cleaning and separation of fractions of compounds. For identification and quantification of compounds we used capillary gas chromatography with FID detection for both families of molecules. The concentrations found within the Bay were relatively small and homogeneous (from 0.1 to 2.6 mg g⁻¹). Cluster analysis suggests three significantly different zones. The indexes used for source identification of hydrocarbons are presented and discussed. Possible origins for these materials are discussed. Similarly, possible explanations are offered on the fluxes suggested by the isophlets. The overall conclusion is that the Bay can be considered as a relatively clean bay with respect to hydrocarbon pollution and that anthropogenic (or even natural) processes have not had a major impact on the Bay.

Key word: Pollution, PAH's, n-hydrocarbons, sediments, Bahía de Todos Santos, México.

RESUMEN

Con el objeto de establecer los niveles base actuales de compuestos aromáticos polinucleares (PAH's) y alifáticos, se determinó la concentración y distribución de tales compuestos en 16 muestras superficiales de sedimentos de la Bahía de Todos Santos, B.C. Se reportan los niveles encontrados. Se utilizó la técnica de extracción en fase sólida (Burrows, 1983) para limpieza y separación por fracciones. La identificación y cuantificación de ambas familias de compuestos se efectuó por medio de cromatografía de gases con columna capilar y con detección por ionización en flama. Las concentraciones encontradas fueron relativamente pequeñas y homogéneas dentro de la bahía (de 0.1 a 2.6 mg g⁻¹). Se efectuó un análisis de grupos que sugiere tres zonas significativamente distintas. Se incluyen índices y se discuten posibles orígenes de estos grupos de hidrocarburos, así como los flujos que sugieren los gradientes de concentración de estos materiales en la bahía. Se concluye que la bahía puede considerarse globalmente como una zona con baja contaminación por hidrocarburos derivados del petróleo o de la combustión, por lo que la influencia antropogénica no es severa hasta la fecha.

Palabras clave: Contaminación, PAH's, hidrocarburos alifáticos, sedimentos, Bahía de Todos Santos, México.

INTRODUCTION

The Bahía de Todos Santos is a body of water located on the Pacific Ocean. In the northwestern state of Baja California Mexico (Fig. 1). Its area is approximately 25,000 Has., with an average depth of 100 m. Oceanographically, this Bay is under the influence of periodical upwelling events and storms in winter. Most of the year, in Ensenada, which is the main city along the bay, the predominant weather is of the mediterranean type. Ensenada has been considered one of the main fishing and commercial ports of Mexico; because of this reason, its ship traffic can be considered constant.

The economy of the region has been sustained by two important and even competing activities, one is the fishing industry and the other, tourism and related activities. Both are potential contributors of alloctonous materials to the sediments of the bay. The main expected materials are organic compounds such as fats and other materials as well as oils, grease, diesel and related materials (Rivera-Duarte 1984; Salas-Flores, 1984).

With a population of approximately 300,000 habitants and a relatively high growth rate, The City of Ensenada generates different sorts of contaminants whose ultimate destination is Bahía de Todos Santos. The main reason for this is the lack of capacity to treat municipal waste water. In fact, the capacity of the waste water treatment plant for the city has been exceeded for the last decade, releasing untreated sewage to the bay. There is also no provision to dispose of the treated water, producing a slow deterioration of the water quality of the bay (Sañudo-Wilhelmy *et al.*, 1985; Martínez-García, 1988) specially within the coastal zone. There are, in addition, other sources of contaminants either due to natural as well as anthropogenic processes, among which we can cite the incomplete combustion of organic materials such as those produce during the burning of chaparral-type vegetation and the fossil fuel consumption. Both processes generate the polyaromatic hydrocarbons (Neff, 1979) that can find their way to the sediments on the bay.

It is considered of primary importance to establish the base levels of these families of pollutants because it is a way to know how the growth in population, with the consequent increase in municipal water discharges, and the possible introduction of other activities in the bay, will affect these levels in the near future. It will also allow the establishment of policies for decision-making such as permissible levels of discharge to the bay. A recent activity that is increasing in the bay has been the construction of

two to three marinas, one of which is already in operation and a second one is under construction.

There are relatively few studies on the organic pollutants that are being introduced to Bahía de Todos Santos (Lizárraga-Partida, 1973; Segovia-Zavala, 1982). At the same time, and although some recent progress has been made, the circulation patterns in the area are still not fully understood.

The information generated is isolated and localized with respect to the levels of hydrocarbons in the bay. For example, information on the levels of hydrocarbons in the Port of Ensenada (Salas-Flores, 1984), where spent oils, diesel, grease and hydrocarbons in general, are frequently discharged. This area can then export these pollutants to the rest of the bay. As consequence of these state of affairs, it is necessary to determine the levels of these two groups of pollutants and to establish its base line levels for the bay. In this sense, we consider it a priority to determine the PAH's levels given that the toxicity, mutagenicity and teratogenicity of these molecules has been clearly established (e.g. Bjørseth and Dennis, 1980; Bemgård *et al.*, 1993; Wenclawiak and Hees, 1994.). These molecules have been reported to form adducts with DNA.

On the other hand, the value of the aliphatic compounds is due to the opportunity to distinguish their possible origins from their chromatographic trace. For example, it is known that individual sources such as phytoplankton, terrestrial plants, and oil spills among others, can be traced from their characteristic "fingerprinting" (Payne, *et al.* 1985; Ehrhardt and Knapp 1989; Kennicut II *et al.*, 1991)

METHODS AND MATERIALS

With the objective of determining the base levels of both aliphatic and polyaromatic hydrocarbons in recent marine sediments of Bahía de Todos Santos, surficial marine sediments were collected during 1994.

This study included 16 stations which were distributed in a systematic fashion in four transects (Fig. 1). These started at the light house located on the Todos Santo's Island and were directed to four different places on the coast. The samples were collected in April 1993. Use was made of a Van Veen drag of 1 Kg capacity. All samples were taken from the center of the sedimentary material and from the top 2 cm. On each occasion, we collected approximately 100 g of sediments. The samples were frozen on board and stored until analysis in the laboratory. On each occasion, a subsample of 100 g was also collected for sediment analy-

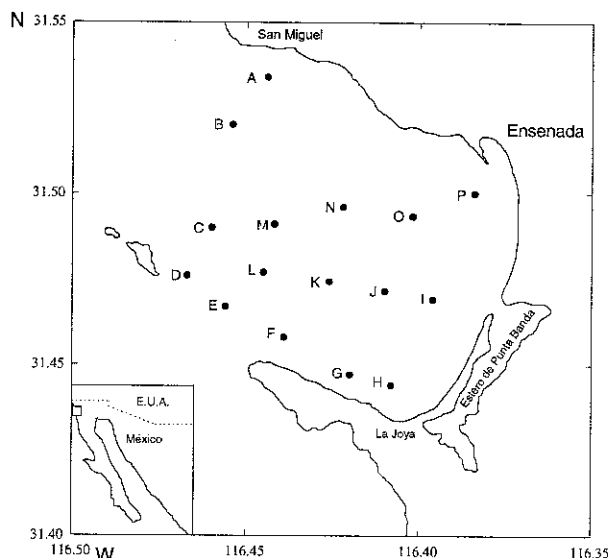


Figure 1. Localization of Bahía de Todos Santos, B.C.

sis such as grain size distribution and organic matter content. Granulometric analysis was carried out according to the technique originally described by Ingram and Galehouse (1971). The percent of organic material was determined according to the procedure described by Loring and Rantala (1992).

The cleaning of all other materials for this analysis included repeated rinses with Micro® detergent in deionized water. All glassware was cleaned by combustion at 400°C for 4 hrs. The extraction procedure was carried out by means of a soxhlet extraction with dichloromethane (Baxter B & J HPLC grade) for 24 hrs. We used 20 g of wet sediment which was mixed with a similar amount of anhydrous Na_2SO_4 as a hygroscopic agent. All extracts were then concentrated by rotoevaporation to a final volume of 10 ml using a controlled temperature of 40°C. To further reduce the extract volume to 2 ml, we used a flow of nitrogen gas (UAP).

The samples were then cleaned and fractionated by the solid phase extraction technique according Burrows (1983). Commercially available 'Sep-Pak' cartridges containing 0.9 g of silica (Baxter B & J) were used. A sequence of 20 ml of pentane, 20 ml of pentane-toluene (70:30 v/v), and 20 ml of toluene (Baxter B & J grade HPLC) permitted us the elution of three fractions which were labeled as F_1 , F_2 y F_3 respectively. The fraction F_1 contained mostly aliphatic hydrocarbons, fraction F_2 contained any n-hydrocarbons not eluted in the F_1 fraction and, when present, the group of molecules collectively referred as the unresolved complex matter (or UCM) which is a group containing branched hydrocarbons. The fraction F_3 contained the aro-

matic fraction as well as other toluene soluble compounds. The quality control included the use of blanks and standard reference sediments (HS-03 National Research Council, Canada) which were analyzed one per set of samples following the same protocol. Percent recoveries for PAH's ranged from 85 to 104%. The compound naphthalene, due to it's higher volatility was recovered in very small percentage, usually <30% by this method.

The hydrocarbon analysis was carried out using a VARIAN gas chromatograph model 3700 equipped with a flame ionization detector (FID). The column used was a DB-5 (J&W Scientific) 30 m long and 0.53 mm ID. The column had a stationary phase thickness of 1.5 μ . The mobile gas phase was hydrogen with a flow of 10 ml min^{-1} . The temperature program consisted of an initial temperature of 70°C which was held isothermal during 2 min and the temperature ramp was set at 10°C min^{-1} to a final temperature of 270°C. This last temperature was maintained for 8 min. The injector and the detector temperatures were set at 250°C and 270°C, respectively.

Standard solutions for each group of compounds were prepared containing the molecules of interest. These solutions were used as external standards for calibration purposes. Each calibration curve was prepared with five concentration levels. The identification was made using the retention times of each compound (t_r). For quantification as well as for the response factor determination, use was made of the integrated signal produced by a Perkin-Elmer integrator model Nelson.

The detection limit (LOD) was calculated for both groups of compounds according to the procedure given Foley *et al.* (1984). The response factor was taken from the calibration curve using the compound with the smallest response factor per family of compounds. All other compounds had smaller detection limits.

The statistical treatment given to this data consisted of a cluster analysis (Wilkinson, 1990) in which each identified compound was included in the calculation. The % organic content of the sample and the size distribution of the sediments were also included as variables within the matrix (Klamer *et al.*, 1990). The inclusion of these variables describes each station more fully. A Z-transformation was conducted previous to the cluster analysis with the objective of removing in-homogeneities between variables.

For the generation of the spatial distributions of both aliphatic and polyaromatic hydrocarbons, we used a geostatistical test that can be described as follows: The organic variables were considered as regionalized variables

and with them, contours were generated. For interpolation, we used an ordinary "kriging" algorithm with a linear variogram and an anisotropy equal to one as a regional average (Davis, 1986).

RESULTS

The calculated detection limits were $0.004 \mu\text{g ml}^{-1}$ for triacontane (C_{30}) and of $0.008 \mu\text{g g}^{-1}$ for the polynuclear aromatics (Benzo(g,h,i)perylene).

There was no evidence of UCM in any station. Although during the analysis, individual compounds were identified and quantified, Table 1 shows only the sum of the concentrations per family of molecules registered on each station. We observed a predominance of aliphatics with relatively high molecular weight as compared to those of low molecular weight. We also noticed the absence of Benz[b]fluoranthene. The concentration profiles did not show gradients with large concentrations near the coast and lower concentrations for stations away from the coast. This precluded the identification of fluxes from point sources on the coast towards the ocean.

Figures 2a and 2b show the observed trends for total aliphatics and total PAH's on the surface sediments of the bay. We observed several important features with respect to the suggested trends and the location of the maximas. The maximas suggest main zones of deposition and also suggest possible sources of these materials, similarly, Fig-

ures 3a and 3b show the distribution of aliphatic and aromatic hydrocarbons respectively, normalized with respect to the % of organic matter present in the sample.

The cluster analysis suggests three separate groups of stations (Fig. 4). One of them (I) included the stations (A and B) in the northern part of the bay (Punta San Miguel) and an extra isolated station (H) located near the Punta Banda Estuary. This group is characterized by showing the smallest concentrations both for the aliphatic ($0.11 - 0.36 \mu\text{g g}^{-1}$) as well as for the aromatic group ($0.46 - 0.71 \mu\text{g g}^{-1}$).

The second group (II), included those stations localized between the Island and Punta Banda which are known to have larger sedimentation rates including the presence of finer particulate material, than the rest of stations. These stations showed the largest PAH's content (1.27 y $1.61 \mu\text{g g}^{-1}$). The concentration of aliphatics in this group varied 0.43 to $1.78 \mu\text{g g}^{-1}$.

The third and last group (III) included most of the station located in the central part of the bay. These stations showed intermediate values in concentration for both groups of compounds, aliphatics were in the range $0.15-2.67 \mu\text{g g}^{-1}$ and the PAH's in the range $0.12-0.80 \mu\text{g g}^{-1}$.

The carbon preference index or CPI (Clark and Blumer, 1967) was used in an attempt to identify the main source or sources of the aliphatic compounds found in the bay (Table 1). It was observed, in general, a certain predominance of even over the odd number of n-hydrocarbons in several of the stations sampled.

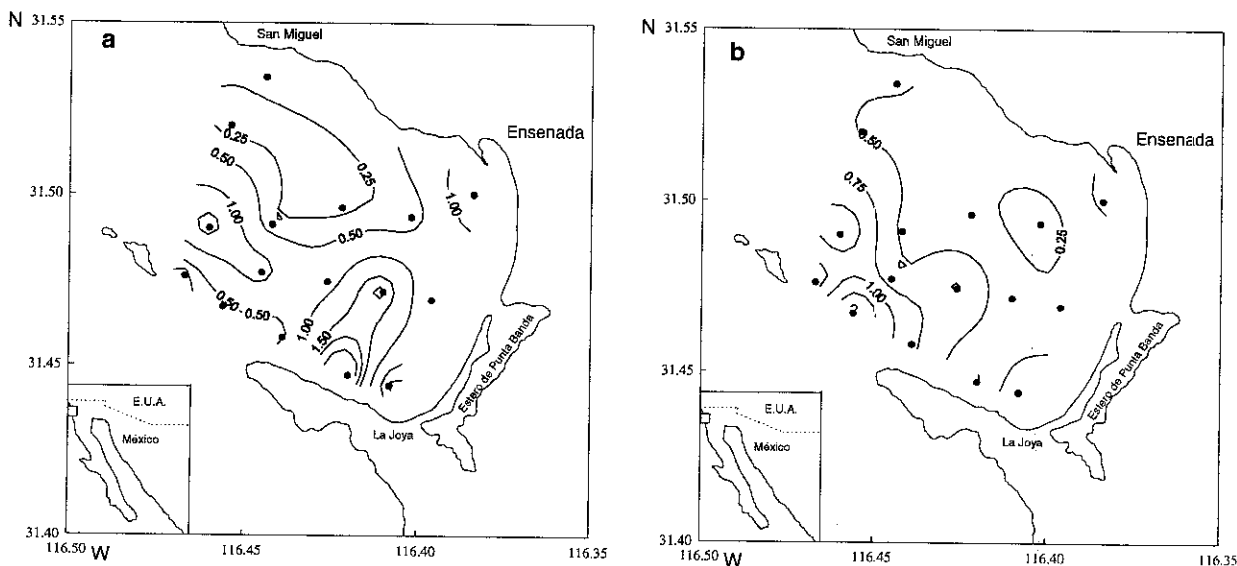


Figure 2. Distribution of the concentration of a) n-hydrocarbons and b) Polyaromatic hydrocarbons in the area (both in $\mu\text{g g}^{-1}$ dry weight).

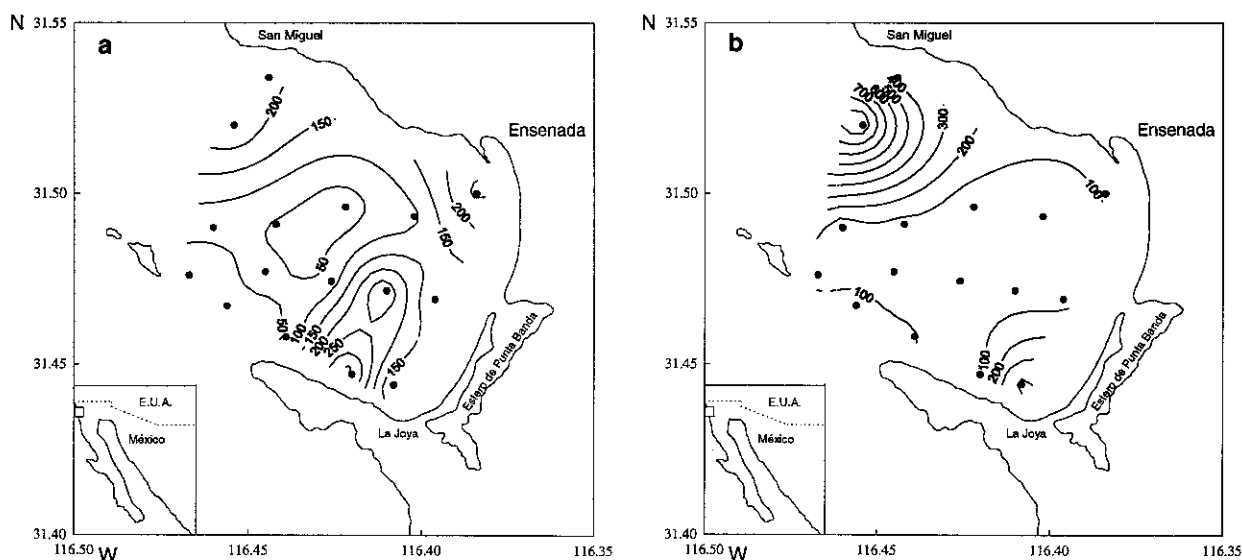


Figure 3. Distribution of a). n-hidrocarburos and b). Poliaromáticos hidrocarburos normalizados con respecto al % de materia orgánica presente en la muestra (en $\mu\text{g g}^{-1}/\%$ materia orgánica).

Two other indexes used for the possible identification of the origin of the polyaromatic hydrocarbons in this work were those of Phenanthrene:Anthracene ratio (Prah *et al.*, 1984), as well as the index of hydrocarbons derived from combustion or COMB, (Brooks *et al.*, 1990) Both indexes are also included in Table 1.

DISCUSSION AND CONCLUSIONS

With respect to the possible meaning of the maxima shown in some of the figures, Figure 2a from station G, for example, we interpret this result as the manifestation of a fault zone which higher than usual temperatures in the water. This in turns produces a movement of water as well as a movement of sedimentary material and organic load associated with them. The other observed maximum, with decreasing concentration towards the center of the bay, most probably suggests the main route of water flow from the ocean during part of the year.

The lower concentrations, found in stations labeled as group I by the cluster analysis, indicate that this zone is one of relatively higher energy which diminishes the trend to sedimentation of particles in this part of the bay, and as a consequence, the hydrocarbons associated with this material. In group II stations, the higher concentrations found clearly suggest the natural deposit area for particulate material in the canyon of Bahía de Todos Santos. This area is probably a good place for preservation of PAH's and other molecules specially those difficult to decompose by bacterial attack.

We understand that the distributions of concentrations of hydrocarbons are the result of physical, biological, chemical and other events. As a consequence, we do not expect to be able to explain the hydrocarbons distributions based

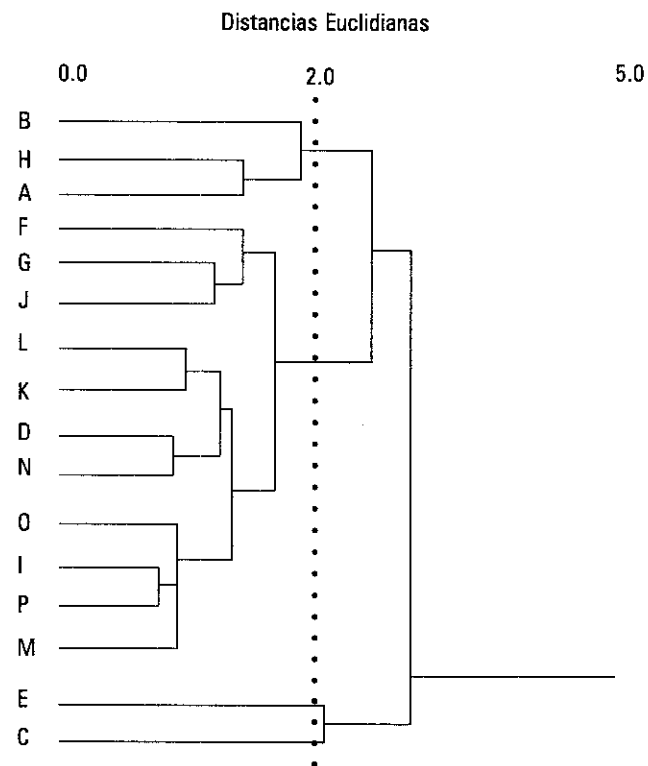


Figure 4. Dendograms showing grouping of stations by similarities.

Table 1. Total concentration of each family of compounds and the indexes calculated for this study.

Station	Aliphatic ($\mu\text{g/g}$)	PAH's ($\mu\text{g/g}$)	% org. matter	% Fr. <63 μm	CPI (11-22)	Pri/phytan e	COMB
A	0.34	0.53	0.16	0.63	0.4		0.9
B	0.11	0.46	0.04	0.14	0.4		15.0
C	1.78	1.26	2.83	95.65	1.3		1.1
D	0.14	0.58	0.86	73.16	1.6		2.9
E	0.44	1.60	1.12	78.29	1.1		1.4
F	0.30	0.79	0.72	23.53	1.5	0.3	4.1
G	2.65	0.20	0.68	23.07	1.4	0.2	3.4
H	0.17	0.70	0.16	2.22	0.3		4.8
I	0.62	0.28	0.58	27.15	1.0	0.8	0.8
J	1.90	0.32	0.62	32.50	1.7		1.9
K	0.69	0.79	1.21	94.68	4.0	0.6	4.2
L	1.24	0.48	1.78	59.13	2.1	0.5	0.9
M	0.25	0.42	0.54	47.27	0.8	2.0	1.0
N	0.16	0.30	0.95	69.60	0.5		1.5
O	0.23	0.13	0.30	14.28	0.6	1.0	0.2
P	1.40	0.57	0.54	42.70	3.0	0.4	1.6

only on the sedimentary patterns such as organic matter content and grain size distributions. In particular, the PAH distributions seem to suggest a lack of clear point sources to the bay sediments. On the contrary, such homogeneous distributions appear to indicate diffuse or non-point sources. It further suggest that the atmosphere is the main route of these molecules.

The CPI's indicate a predominantly petrogenic source of the aliphatic found in Bahía de Todos Santos sediments. However, in some stations, it was possible to notice a predominance of marine biosynthetic materials suggesting an autochthonous origin.

There were discrepancies found among the indexes utilized in this work. For example, between the phenanthrene:anthracene ratio and the COMB index, those indexes suggested opposite origins for the materials. This fact leads to the conclusion that both the petrogenic and atmospheric routes played similar roles with respect to the importance of their contribution to most stations. We have concluded that the atmospheric route is the main route of entry of PAH's and that the homogeneous distribution indicates the non-point source character of the introduction of these materials.

With respect to the aliphatic molecules, the absence of the chromatographic feature known as unrecognized carbon matter (UCM) indicates that there have been no recent oil spills of importance (Payne *et al.*, 1985) in the bay or near the bay area.

A comparison of the results obtained in this study with those reported by similar studies in other areas (e.g. Steinhauer and Boehm, 1992. Moyano *et al.*, 1993) strongly indicates that there is no significant oil pollution problem in the Bahía de Todos Santos area. In addition, the concentration levels found for PAH's are lower than those reported by GESAMP (1993) which have been demonstrated to be toxic at least to one of the species tested. In general, it can be concluded that the Bahía de Todos Santos, is relatively unpolluted and, at present, free of hydrocarbon's pollution.

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