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Survey of petroleum aromatic hydrocarbons in the São Sebastião Channel, SP, Brazil, November 1985 to August 1986

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- *Abstract*: A survey of the petroleum aromatic hydrocarbons levels on the surface waters of the São Sebastião Channel, São Paulo, Brazil is presented. The survey was done in order to assess the influence of the biggest maritime oil terminal of Brazil on the petroleum hydrocarbons levels of the area. Fourty four samples taken from 1 m depth were analysed by fluorescence spectroscopy. The highest level, 45.29 $\mu g.l^{-1}$, was found on the side of an anchored tanker and the lowest detectable level was 0.19 $\mu g.l^{-1}$.

- *Descriptors*: Pollution survey, Aromatic hydrocarbons, Tankers terminals, Fluorescence spectroscopy, São Sebastião Channel, Brazil: São Paulo.

- *Descritores*: Poluição petrolífera, Hidrocarbonetos aromáticos, Terminais petrolíferos, Espectroscopia de fluorescência, Canal de São Sebastião: SP.

Introduction

The biggest oil terminal in Brazil is located at the São Sebatião Channel, São Paulo State. In 1985 it received 624 ships, carrying 36 millions cubic meters of oil and derivatives (PETROBRÁS, 1986). The Channel is 25 km long, with a varying width from 2 to 6 km and presenting depths between 20 and 25 m at the entrances and up to 40 m at the central part. Therefore it is an exceptional natural port for oil tankers up to 300.000 tons.

The terminal Almirante Barroso (TEBAR) is in operation since 1967 and numerous oil spills have already occurred in the area. Probably the worst of all spills was the one of the "Brazilian Marina" tanker in 1978. In this event about 6000 cubic meters of oil were spilled in the Channel. Due to the strong currents, values up to 1.4 knots (Furtado, 1978), the oil spread towards north covering many beaches, damaging the shellfish cultures and shrimp and sardine fishing activities.

In the last ten years many other small spills and two punctures in the pipeline, which runs parallel to the coast line, occurred leading to a constant input of anthropogenic hydrocarbons in this environment. In the absence of published data about the aromatic hydrocarbons levels at the surface waters of the area, we performed a fluorescence spectroscopy survey program between November 1985 and August 1986.

Study area, sampling and analytical procedure

The study area and the sampling sites of sub-superficial water collected at 1 m depth are shown in Figure 1. Four sets of 11 samples were collected between November 1985 and August 1986 along the Channel. Sampling and extraction procedures followed IOC/UNEP (1984) methodology with the modifications of Ehrhardt (1983) in the removal of the n-hexane extract from seawater. The fluorescence spectrophotometric determination is sensitive to polycyclic aromatic hydrocarbons, which are fairly abundant in petroleum, but not to biogenic hydrocarbons which are normally aliphatic or olefinic.

N-hexane was pesticide grade reagent from Merck Art 4371. Sodium sulphate analytical grade Baker was Soxhlet extracted with ethanol, n-hexane and finally kiln fired at 450°C for three hours. All glassware and the sampling bottles were carefully cleaned by washing with detergent solution, followed by rinsing with distilled water, distilled ethanol and a final rinse with n- hexane.

To avoid a possible oil plume from the vessel when on station, sampling was done on the bow of the ship and immediately after stopping. Water was collected from 1 m depth with 2 liters glass bottles mounted on a weighted

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frame. The bottle had a glass stopper that was pulled by a nylon rope at the sampling depth. Samples were extracted twice with 25 ml of n-hexane, on the same bottle, by vigorous vortex mixing for 15 minutes. The combined n-hexane extracts were dried with sodium sulfate and concentrated on a rotary evaporator. Final volume was adjusted to 5 or 10 ml in a volumetric flask. Fluorescence levels were measured on a Perkin-Elmer LS-5 spectrofluorometer. Excitation was at 310 nm and the fluorescence at 360 nm was recorded. Total aromatic hydrocarbon concentration were determined as oil equivalents against a calibration curve of Carmopolis crude oil, which was artificially weathered by distillation, topping at 180°C.

Reagent blanks were made with 50 ml n-hexane rinses of the sampling bottles taken through the analytical procedure above. Field blanks were done by conducting a third and a fourth extraction of the seawater already extracted (Knap *et al.*, 1986).

An intercomparison exercise in Bermuda conducted by IOC/UNEP experts (Knap *et al., op. cit.*) showed that the

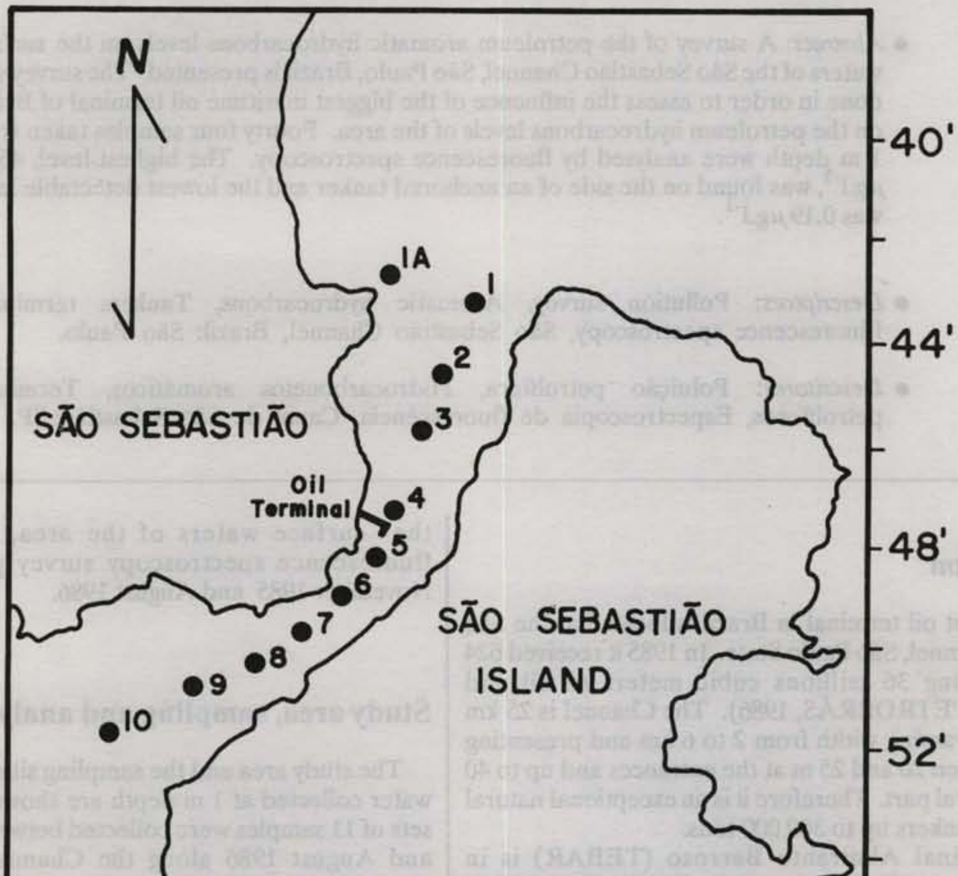

Fig. 1. Sampling location.

fluorescence method has a good precision with an average 60% relative standard deviation.

Results and discussion

Results of the survey given as oil equivalents are shown in Table 1. Dissolved/dispersed hydrocarbon levels show a wide range of concentration depending on the sampling period and on the sampling point. The highest value was registered on Station 6* with 45.29 $\mu g.l^{-1}$. This sample was taken on the side of a tanker which was emanating continuously oil, forming an iridescent sheen on the surface.

The oil terminal is located between Stations 4 and 5, as shown in Figure 1, but these stations does not always present the highest values for the aromatic hydrocarbons.

In November 1985 only Stations 1 and 8 presented levels between 1 and 2 $\mu g.l^{-1}$, indicating absence or very low oil pollution (Marchand, 1980; Law, 1981). All other sampling points showed levels above 2 $\mu g.l^{-1}$, which are characteristic of oil pollution.

In opposition, in February 1986 the highest levels of aromatic hydrocarbons were found in the south west part of the Channel. Stations 2 and 3 correspond to very clean seawater but Station 6 presented a high level of oil pollution with 8.82 $\mu g.l^{-1}$.

In May 1986 the picture is similar to November 1985 because we found measurable levels of aromatics in all stations. This time the highest level was found on the northern part of the Channel on Station 1A and 1. All stations presented values above 1 $\mu g.l^{-1}$ with the majority over 2 $\mu g.l^{-1}$.

Finally, in August 1986 we apparently had a situation of a very clean environment with respect to oil pollution. With the exception of sample 2 all stations presented values below 1 $\mu g.l^{-1}$.

Some samples were done in duplicate to test the precision of the method. The relative standard deviation is 12.15%. The total error of the method is given by the expression of Mac Farren *et al.*, (1970) where:

Total Error = Relative Error + 2 (Relative Standard Deviation)

Relative Error : 4% and Total Error = 28.31 % in our analytical procedure. Practical limit of detection depends on the final volume of the extract. For 10 ml it is 0.18 $\mu g/l$ of oil.

Although once oil is dispersed in seawater it immediately suffers alteration in its initial composition due to evaporation, microbial action and photochemical reactions, the fluorescence method is still a useful and relative simple and inexpensive tool to assess oil contamination. However, the wide spatial distribution and weathering effects plus microbial and photochemical action can make quantitative analysis less meaningful. The fluorescence technique does not permit to draw any conclusions about the weathering, microbial or photochemical processes that have altered the original oil composition once it is spilled. It is necessary to analyze the seawater soluble oil fraction by gas chromatography coupled to mass spectrometry to get the extension of the above processes.

The large variations of the levels in São Sebastião are obviously due to the complex local surface circulation, which can vary from situations of intense currents to absolute calm periods, associated with the local oil inputs from the terminal operations and oil tankers.

Castro Filho (1990) already pointed out that the currents in the Channel of São Sebastião may be highly variable in

Table 1. Aromatic hydrocarbons levels in São Sebastião Channel, São Paulo, Brazil

Station	$\mu g.l^{-1}$ oil equivalents as Carmopólis crude oil			
	November/85	February/86	May/86	August/86
1A	-	0.85	4.58	0.58
1	1.18	0.88	3.66	0.24
2	2.76	nd	2.25	1.34
3	3.37	nd	1.93	0.26
4	2.49	nd	2.37	0.28
5	3.67	2.82	1.77	0.32
6	2.43	8.52	1.93	0.25
7	5.25	2.58	3.13	0.25
8	1.79	1.45	2.13	0.19
9	5.37	1.39	2.25	0.21
10	4.89	nd	2.33	0.74
6*	45.29	-	-	-

Relative Mean Standard Deviation = 12.15%

Relative Error = 4.01%

Total Error : Relative Error + 2 SD = 28.31%

space in time, specially during periods of weak winds, therefore any extrapolation of current data in space and time for environmental purposes is meaningless.

Based on current speed measurements, current drifters trajectories and sediment distribution Furtado (1978) presented a general circulation pattern for the Channel. In another study Furtado *et al*. (1987) presented a scheme for the oils spills drifts which is shown in Figure 2. Castro Filho (1985) applied a barotropic nested model to study wind driven circulation in the South Brazilian Bight. .He also studied the wind driven current of the São Sebastião Channel during the winter (Castro Filho, 1990) concluding that there is a significant correlation between wind and currents along the Channel and that currents are predominantly to the northeast. Current reversals occur due to meterorological disturbance passages.

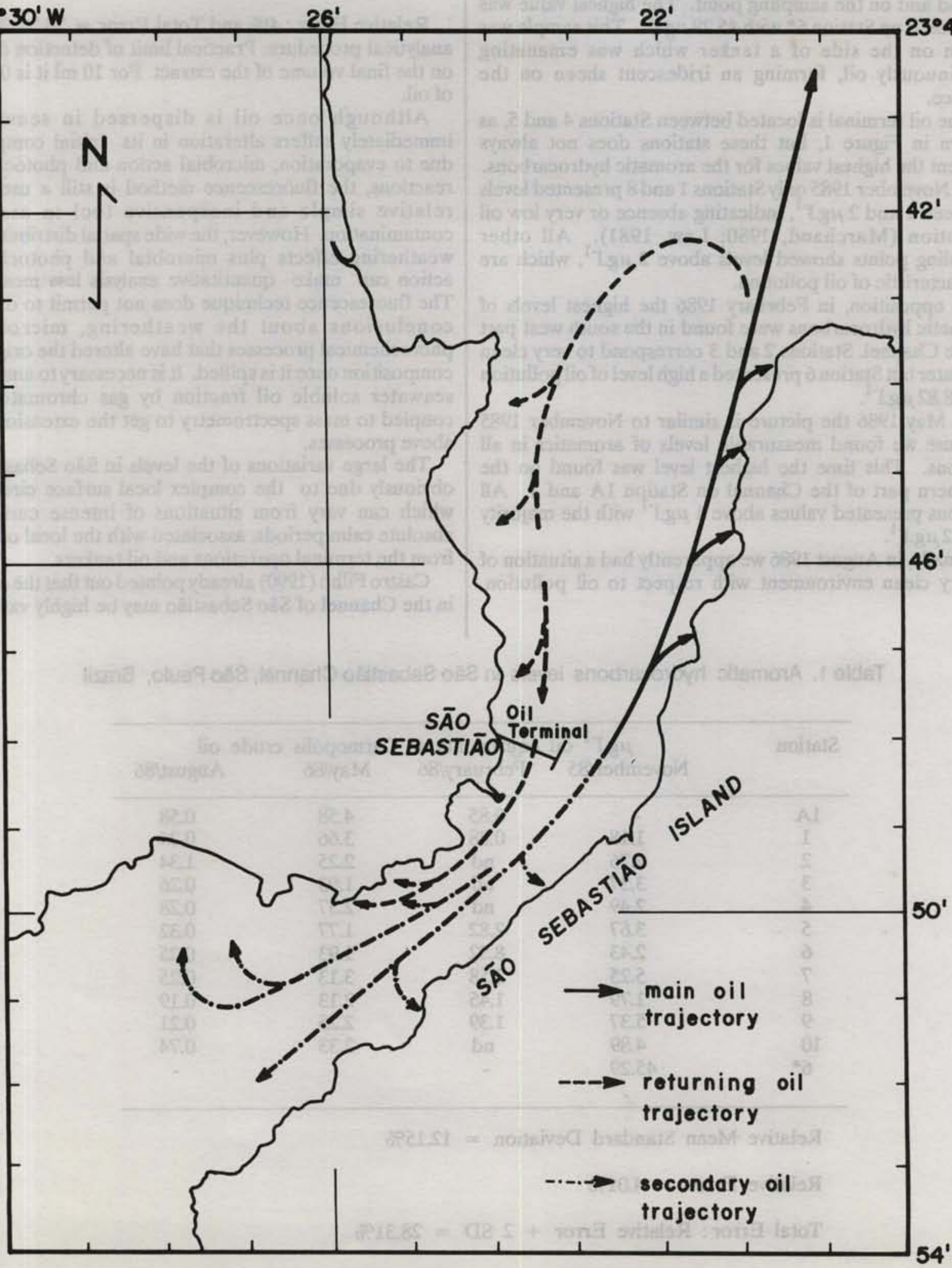

Fig. 2. Scheme for the oil drift on the São Sebastião Channel (according to Furtado *et al*., 1987).

All this studies show that the currents are mainly wind driven and that the prevailing trajectories for oil spills is northeast but the oil can also drift to the south west part of the Channel. Further studies are been made on ongoing projects by Castro Filho* to elucidate the local circulation pattern more precisely in order to make more accurate predictions of oil spill trajectories.

Conclusions

The petroleum aromatic hydrocarbon levels in São Sebastião Channel in the period of study were highly variable due to the variable oil inputs of the TEBAR and to the variations of the local surface circulation. The present work is a survey, limited in space and time, with the aim of identifying hot spots of oil pollution and possible trends in the levels associated to local surface circulation.

An important aspect showed by our fluorescence data is that, depending on the sampling schedule, levels of oil pollution present wide variations. This can led the decision makers and environmentalists to draw false conclusions about the study area. Therefore the need of a regular sampling schedule, in any monitoring study of hydrocarbons in coastal zones, cannot be overemphasized if we want to assess the extent of the anthropogenic oil inputs.

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Resumo

Foi realizado um levantamento dos níveis de hidrocarbonetos do petróleo em águas superficiais do Canal de São Sebastião, São Paulo, Brasil. Esse levantamento foi feito para avaliar a influência de hidrocarbonetos do petróleo do maior terminal de óleo do país. Foram coletadas 44 amostras a 1 m de profundidade, extraídas em n-hexano e analisadas por espectrofluorescência. O ponto de maior concentração, 45,29 $\mu g.l^{-1}$, foi coletado ao lado de um navio petroleiro ancorado na região, e o menor valor detectado foi de 0.19 $\mu g.l^{-1}$ proveniente da parte sul do Canal.

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