Bull. Environm. Contam. Toxicol. 28, 166–171 (1982)

Analysis of Environmental and Tar Samples from the Nearshore South Texas Area After Oiling from the Ixtoc-1 Blowout

C. A. Bedinger, Jr.[1] and C. P. Nulton[2]

[1]*Office of Planning and Program Development, Southwest Research Institute, 2200 West Loop South, Houston, TX 77027, and* [2]*Department of Environmental Sciences, Division of Chemistry and Chemical Engineering, Southwest Research Institute, P.O. Drawer 28510, San Antonio, TX 78284*

The blowout of the exploratory oil well Ixtoc-1 in the Bay of Campeche, Mexico resulted in the largest oil spill in the history of offshore oil production. Numerous sources cite the volume of discharge of 10,000 to 50,000 barrels per day with a total spill of up to three million barrels. An estimated three million gallons of this oil found its way to South Texas beaches from the Rio Grande to Pass Cavallo.

Near-shore environmental samples and tarballs collected from three locations on the Texas coast (April 22 to May 1, 1980) were analyzed by capillary GC/MS in an attempt to determine the nature and extent of residual contamination of this area resulting from the blowout. Focus was on aromatic constituents due to their toxicity (ANDERSON et al. 1974) and solubility.

THE STUDY AREA

Figure 1 shows the South Texas coast and the three locations that were sampled. Site 1, five miles south of Port Aransas, was chosen to represent an area of minimal oiling and coincides with a sampling location being used by several other researchers doing beach studies (FLINT 1980). Site 2, approximately 12 miles north of the Port Mansfield jetties, is the area where littoral tarmats, between the shore and the first sand bar, were described (WOODS 1980). This site was in the area of highest concentration of tarballs along North Padre Island. Site 3, approximately 12 miles south of the Port Mansfield jetties, was in the area of highest concentration of tarballs on South Padre Island. During this sampling, no exposed tarmats were seen except in an area between the southern Port Mansfield jetty and the beach. Many tarballs, both floating and collected from the bottom, were observed at Sites 2 and 3.

METHODS AND MATERIALS

Sampling. Sediment core samples, 5 cm in diameter and 10 cm deep, were taken with a Pugh-Baker corer (BAKER et al. 1977). Undisturbed surface sediments were collected with a Peterson grab. Sediments were placed into acid-washed, hexane-rinsed 16-oz glass jars and frozen until processed. Water samples were taken approximately 0.3 m under the surface with acid-washed, hexane-rinsed one-gallon bottles (opened and closed under the surface); the bottles

0007-4861/82/0028-0166 $01.20

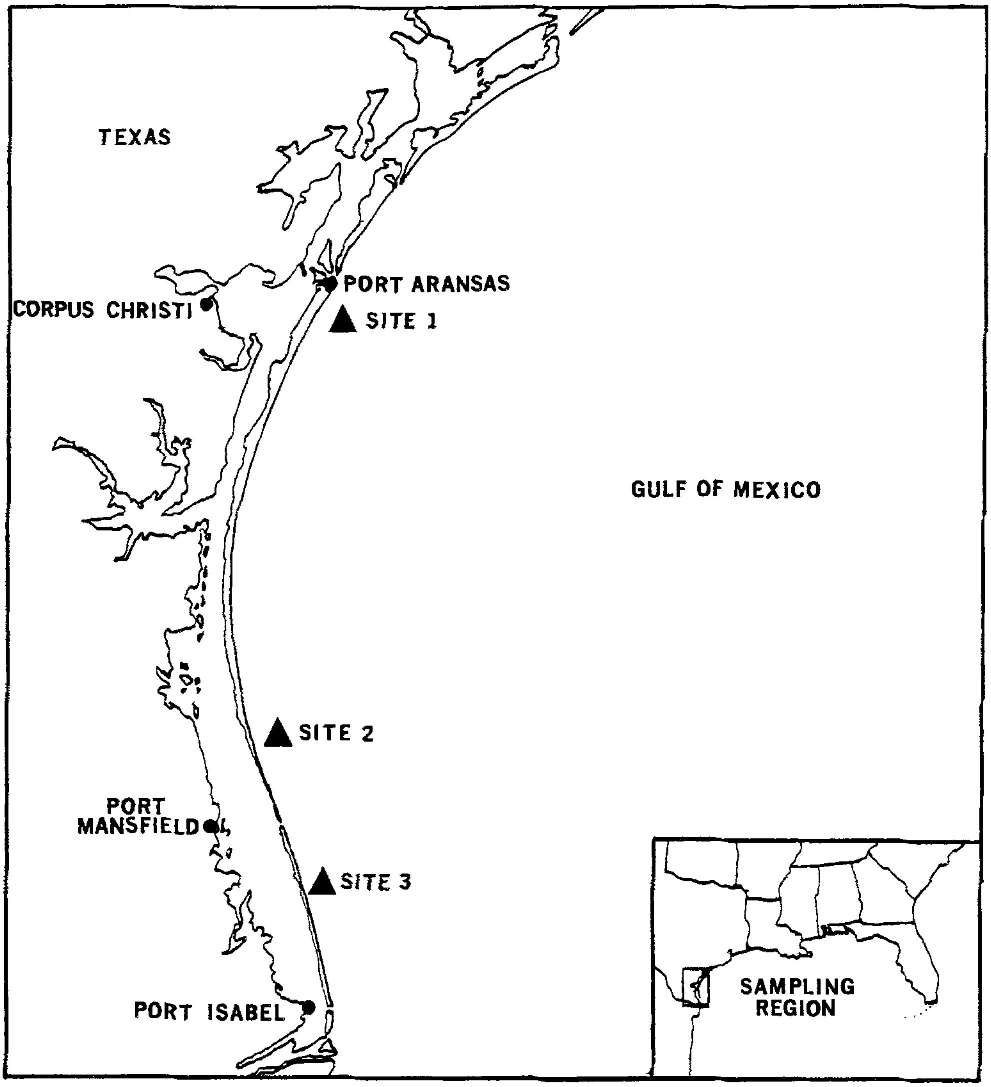

Figure 1. South Texas Coast; Sampling Sites are Shown

were refrigerated immediately. The coquina clams (Donax variabilis) were collected by hand in the surf zone; trawls were used to collect the white shrimp (Penaeus setiferus), the blue crab (Callinectes sapidus) and the silver seatrout (Cynoscion arenarius). Organisms were frozen immediately in clean glass jars or in hexane-rinsed aluminum foil. These fauna were intimately associated with deposits of tarballs on the bottom at locations where the latter occurred.

Preparation of Extracts. One liter water samples were microextracted with 500 μL hexane (RHOADES and NULTON 1980). Sediments (50 g) were mixed with sodium sulfate and Soxhlet extracted with benzene for 16 hours. The extracts were first concentrated to 1 mL by the Kuderna-Danish method; after adding an internal standard

(d_{10}-anthracene), the extract was further concentrated to 100 µL with a stream of chromatographic grade nitrogen.

Pooled tissue samples were minced by hand and digested in a 4N KOH/60% methanol (v/v) solution for 48 hours. The digest was then extracted three times with 20 mL of 15% dichloromethane/hexane (v/v). The emulsion was broken each time by centrifuging at 2000 RPM for 20 minutes. The combined extracts were concentrated and the internal standard added as described above for the sediments.

GC/MS Analysis. GC/MS analysis was performed on a Finnigan Model 3300F equipped with a Grob-type capillary column injector and an SE-54 fused silica capillary column (30 m x 0.2 mm). The column was temperature programmed from 80 to 280°C at 8°C/minute and held at final temperature for ten minutes. Aromatic compounds searched for by generating an extracted ion current profile for the appropriate ions included: ethylbenzene, xylenes, naphthalene, dimethylnaphthalenes, phenanthrene, anthracene, dimethyl- and ethylphenanthrenes and anthracenes, fluoranthene, pyrene, chrysene, benzo(a)pyrene, perylene, dibenzo(g,h,i)perylene, methyldibenzothiophenes, and dimethyl- and ethyldibenzothiophenes.

A standard containing these compounds were run twice daily with each set of analyses.

RESULTS AND DISCUSSION

Two distinct types of tar, "soft" and "hard," were found at all sites; however, as previously mentioned, tar was particularly abundant at Sites 2 and 3. Selected physical and chemical features of each type are summarized below in Table 1.

TABLE 1. Selected Physical and Chemical Features of "Soft" and "Hard" Tar

Feature	"Soft" Tar	"Hard" Tar
Physical description:	dull brown to black; crumbly, contains much sand and other inclusions; irregular shapes; 0.5-5 cm in diameter.	shiny black inner surfaces, homogeneous in appearance; does not contain sand or inclusions; flat irregular shapes; small flecks to 10 cm in size.
Selected Constituents (ppm, w/w)		
naphthalene	<0.5	15
phenanthrene	40	8
n-pentadecane	430	4
n-heneicosane	950	<0.5
n-octacosane	720	<0.5

These data along with the total ion current chromatograms of the two types of tar (Figure 2) indicate that the "hard" tar is the more weathered of the two. The two tars appear to have been formed differently. The soft tar may be derived from mousse which has mixed with sand, trash, small organisms, etc., whereas the hard tar, which has no inclusions, is probably formed at sea.

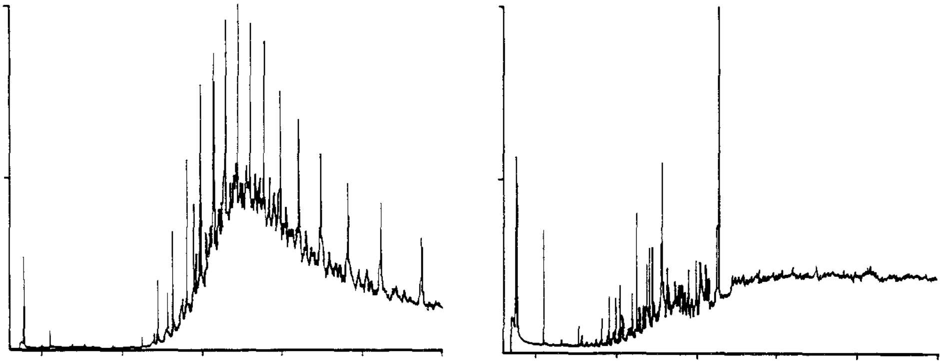

Figure 2. Reconstructed Ion Chromatograms of Soft Tar (right) and Hard Tar (left)

Similarities found between the "hard" and "soft" tars which indicate their common origin in Ixtoc oil include the dimethyl/ethyldibenzothiophene series (Figure 3), the trimethyl/methylethylnaphthalene series (Figure 4), and the ^{13}C stable isotope ratios (Table 2).

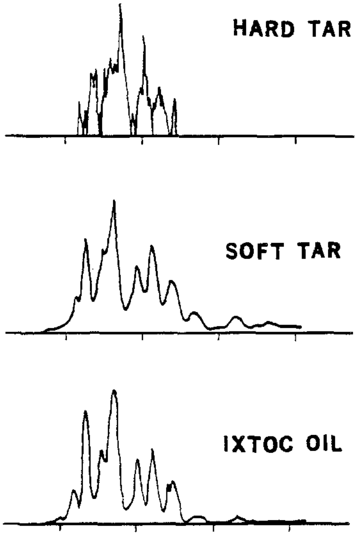

Figure 3. Extracted Ion Current Profile of Mass 212 (base peak of dimethyl/ ethyldibenzothiophenes)

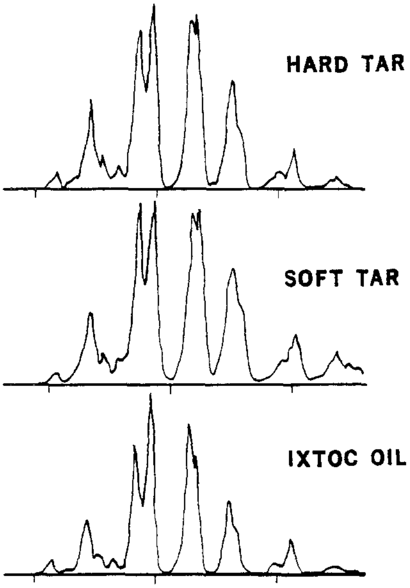

Figure 4. Extracted Ion Current Profile of Mass 170 (base peak of trimethyl/ methylethylnaphthalenes)

TABLE 2. Stable Isotope Ratios for Ixtoc Oil, Mousse, and Hard and Soft Tar

Fraction	del ^{13}C* Ixtoc Oil	del ^{13}C* Weathered Mousse	del ^{13}C* Soft Tar	del ^{13}C* Hard Tar
Whole Oil	-27.3			
Saturates	-27.7	-27.4	-27.3	-27.4
Aromatics	-27.1	-26.9	-26.7	-26.8
Polar	-26.8	-26.7	-26.6	-26.6

* Relative to PDB carbonate standard.

The results of near-shore environmental analysis for aromatic petroleum constituents are shown in Table 3.

TABLE 3. Aromatic Compounds in Near-Shore Environmental Samples

Sample Type	Site	Wet Wt (g)	Aromatic Compounds (ppb, wet wt)
Water	1		ND
Water	2		ND
Water	3		ND
Sediment	1	50	naphthalene;* acenaphthene;* dimethylnaphthalenes*
Sediment	2	50	naphthalene;* acenaphthene;* anthracene*
Sediment	3	50	naphthalene ;* dimethylnaphthalenes;* acenaphthene*
White Shrimp	1	35	ND
White Shrimp	1	68	ND
White Shrimp	2	80	ND
White Shrimp	2	96	fluoranthene*
White Shrimp	3	106	anthracene;* acenaphthene*
White Shrimp	3	107	ND
White Shrimp	3	83	ND
White Shrimp	3	91	ND
Coquina Clam	1	17	chrysene*
Coquina Clam	2	11	acenaphthene;* dimethylnaphthalene;* anthracene*
White Shrimp ovary	3		ND
White Shrimp digestive gland	3		ND
White Shrimp tail muscle	3	9	ND
Silver Seatrout	1	25	ND
Silver Seatrout	3	25	ND
Silver Seatrout	3	25	ND

* Trace amount; less than detection limit

ND - not detected.

Detection limits were 1 µg/L in water, 10 ng/g in sediment, and 10 ng/g in biota.

Generally, water, sediment, and tissue samples contained little or no detectable concentrations of aromatic contaminants. It is emphasized that although substantial amounts of tar were observed at Sites 2 and 3, the original oil coating the Texas beaches had been blown away nearly seven months prior to sampling. During this time, any aromatic hydrocarbon contamination, which may have existed immediately after the appearance of the oil on the beaches (August 1979), had been dissipated (diluted, metabolized, etc.). Since the remaining tar contained relatively low levels of soluble aromatic hydrocarbons and the near-shore sediments were very sandy (95 to 98%), there was no continuing influx of these compounds into the near-shore environment.

ACKNOWLEDGEMENTS

This work was supported by Southwest Research Institute. The stable isotope analyses were performed by Coastal Science Labs, Port Aransas, Texas. The authors thank Sue R. Durke for her technical assistance.

REFERENCES

BAKER, J. H., K. T. KIMBALL, and C. A. BEDINGER, Jr.: Water Res 11, 597 (1977).

FLINT, R. W.: Personal communication, University of Texas, Mar. Sci. Inst., Port Aransas, Texas.

RHOADES, J.W. and C. P. NULTON: J. Environ. Sci. Health 5, 467 (1980).

WOODS, J.: Nat. Park Service, personal communication, Padre Island Nat. Seashore 94052, South Padre Island Drive, Corpus Christi, Texas, 78418